

A Reactive Intermediate, $[\text{Ni}_5(\text{C}_6\text{H}_4\text{N}_3)_6(\text{CO})_4]$, in the Formation of Nonameric Clusters of Nickel, $[\text{Ni}_9(\text{C}_6\text{H}_4\text{N}_3)_{12}(\text{CO})_6]$ and $[\text{Ni}_9(\text{C}_6\text{H}_4\text{N}_3)_{12}(\text{CO})_6].2(\text{C}_3\text{H}_7\text{NO})$

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Abstract. Three new molecular compounds, $[\text{Ni}_5(\text{bta})_6(\text{CO})_4]$, **I**, $[\text{Ni}_9(\text{bta})_{12}(\text{CO})_6]$, **II**, $[\text{Ni}_9(\text{bta})_{12}(\text{CO})_6].2(\text{C}_3\text{H}_7\text{NO})$, **III**, (bta = benzotriazole) were prepared employing solvothermal reactions. Of these, **I** have pentanuclear nickel, whereas **II** and **III** have nonanuclear nickel species. The structures are formed by the connectivity between the nickel and benzotriazole giving rise to the 5- and 9-membered nickel clusters. The structures are stabilised by extensive $\pi \dots \pi$ and C-H... π interactions. Compound **II** and **III** are solvotamorphs as they have the same 9-membered nickel clusters and have different solvent molecules. To the best of our knowledge, the compounds **I–III** represent the first examples of the same transition element existing in two distinct coordination environment in this class of compounds. The studies reveal that compound **I** is reactive and could be an intermediate in the preparation of **II** and **III**. Thermal studies indicate that the compounds are stable upto 350°C and at higher temperatures (~800°C) the compounds decompose into NiO. Magnetic studies reveal that **II** is anti-ferromagnetic.

Keywords. Metal complex; nickel; benzotriazole; nickel carbonyl; crystal structure; structural transformation.

1. Introduction

The usefulness of coordination chemistry in the discovery of new and important solids has been well established during the last two decades. A new family of compounds, known as inorganic coordination polymers (CP) or metal-organic framework (MOF) compounds, resulted due to the intense pursuit by many researchers.¹ A clever combination of the guiding principles of inorganic coordination chemistry along with the functionality of organic chemistry was responsible for the synthesis of this unique class of compounds. Coordination chemistry principles were employed in the stabilization of polymetallic structures. Thus, interesting polyoxometallic clusters such as Keggin ion,² Anderson ion,³ etc., have been prepared and characterized. Organic ligands were also employed in the stabilization of polyoxo metal clusters based on molybdenum forming interesting structures.⁴ Though polyoxo metal clusters of different nuclearity have been known for a long time,⁵ the discovery of single molecular magnet behaviour in the manganese compound,

$[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ (R = Me, Ph),⁶ renewed much interest in this class of compounds. Cronin and co-workers expanded this family of compounds to include many new heterometallic clusters.⁷ New molecular cluster compounds based on transition metals have been prepared and examined for their interesting physical and chemical properties.⁸ Presently, we examined the formation of polyoxo metallic compounds based on nickel. During the course of this study, we have isolated three compounds, $[\text{Ni}_5(\text{bta})_6(\text{CO})_4]$, **I**, $[\text{Ni}_9(\text{bta})_{12}(\text{CO})_6]$, **II**, $[\text{Ni}_9(\text{bta})_{12}(\text{CO})_6].2(\text{C}_3\text{H}_7\text{NO})$, **III** (bta = benzotriazole) having five (**I**) and nine (**II**, and **III**) nickel species, respectively. More importantly, we have established that the five-membered compound, $[\text{Ni}_5(\text{bta})_6(\text{CO})_4]$, **I**, could be reactive and a possible intermediate in the formation of the nine-membered compound, $[\text{Ni}_9(\text{bta})_{12}(\text{CO})_6]$, **II**. In this paper, we present the synthesis, structure and related studies.

2. Experimental

All the compounds were prepared employing solvothermal method. A reaction mixture of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

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(0.036 g, 0.125mM) and benzotriazole (bta) (0.018 g, 0.15mM) was dissolved in 6 mL of dimethyl formamide (DMF), and homogenized at room temperature. The mixture was transferred into a 23 mL PTFE lined stainless steel autoclave and heated to 150°C and 180°C for 72 h, independently. The same reaction mixture was employed for the preparation of all the three compounds. At lower temperature, (150°C), a mixture of products (predominantly **I** and **II**, with small amounts of **III**) were formed and at higher temperature (180°C), only **II** was formed. The products, dark blue coloured block shaped crystals (**I** and **III**) and rod shaped crystals (for compound **II**), were filtered under vacuum, washed with DMF and dried at ambient conditions. We have synthesized compound **I** in pure form with a small yield in only one of the attempts. Compound **III** on the other hand, could not be obtained as a pure phase.

Since only compound **II** could be prepared as a pure phase, it was characterized by powder X-ray diffraction (PXRD), IR, UV-vis and thermogravimetric analysis (TGA). The purity of Compound **I**, prepared in one of attempts was also confirmed by the PXRD. The PXRD was recorded in the 2θ range of 5–50° using Cu K α radiation (Philips X'pert). The observed PXRD patterns of **I** and **II** were consistent with the simulated XRD patterns generated based on the structures determined using the single crystal XRD studies (figures S1 and S2). The infrared (IR) spectroscopic study was carried out in the mid – IR range using KBr pellets (Perkin-Elmer, SPECTRUM 1000). Compound **II** exhibited sharp and characteristic IR bands. Presence of a weak band at $\sim 993\text{ cm}^{-1}$ and a sharp band at $\sim 1200\text{ cm}^{-1}$ were assigned to the C-H out of plane bending and C-H in plane bending modes along with triazole ring breathing mode. A strong peak at $\sim 1789\text{ cm}^{-1}$ could be due to the terminal C=O (figure S3). Similar IR bands have been observed before.^{9,10}

Room temperature UV-Vis spectroscopic and photoluminescence studies have also been carried out (figure S4–S6). Thermogravimetric analysis (TGA) (Mettler-Toledo) was carried out in an oxygen atmosphere (flow rate = 50 mL/min) in the temperature range 30–850°C (heating rate = 5°C/min) (figure S7). The TGA studies indicated that **II** was stable up to $\sim 370^\circ\text{C}$. The compound exhibited one weight loss of $\sim 77.5\%$ in the broad temperature range of 370–610°C, which corresponds to the loss of benzotriazole and carbonyl groups (calc. 75%). The final calcined product was found to be NiO by PXRD (JCPDS: 89-5881) (figure S8).

Magnetic measurements were carried out in the temperature range of 2–300K employing a Quantum Design MPMS-XL SQUID magnetometer.

2.1 Single crystal structure determination

A suitable single crystal of each compound was selected under a polarizing optical microscope and glued to a thin glass fibre. The single crystal data were collected at 120(2) K for all the compounds on an Oxford Xcalibur (Mova) diffractometer equipped with an EOS CCD detector. The X-ray generator was operated at 50 kV and 0.8 mA using Mo K α ($\lambda = 0.71073\text{ \AA}$) radiation. The cell refinement and data reduction were accomplished using CrysAlis RED.¹¹ The structure was solved by direct methods and refined using SHELX97 present in the WinGX suit of programs (version 1.63.04a).¹² All the hydrogen positions were initially located from the difference fourier map and included at geometrically ideal position and refined in the riding mode. The full matrix least-squares refinement against $|F^2|$ was carried out using WinGx package of programs.¹³ The final refinements included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. The detailed structural and the refinement parameters are presented in table 1. Important bond distances are listed in table 2. The CCDC numbers for the compounds are 999036 for **I**, 999037 for **II**, and 999038 for **III**.

3. Result and Discussion

3.1 Structure of $[\text{Ni}_5(\text{C}_6\text{H}_4\text{N}_3)_6(\text{CO})_4]$, **I**

Compound **I** contains 21 non-hydrogen atoms in its asymmetric unit, of which three nickel atoms are distinct (figure S9). All the nickel atoms Ni(1), Ni(2) and Ni(3) occupies special position ($2d$), ($2d$) and ($6i$) with site multiplicities of 0.16, 0.16 and 0.5, respectively. While Ni(1) has a distorted octahedral geometry, Ni(2) and Ni(3) have distorted tetrahedral geometry formed by the nitrogen and the C atoms of benzotriazole and [C=O] groups. The tetrahedral Ni(2) and Ni(3) are connected to three nitrogen atoms of benzotriazole and one carbon atom of the [C=O]⁻ group. The octahedral nickel, Ni(1), is coordinated with six nitrogen atoms from six different benzotriazoles ligands (figure 1). The average distance between the terminal tetrahedral nickel centers was found to be 5.891 Å, while that between the octahedral and the tetrahedral nickel was 3.606 Å.

The nickel centres are connected through the benzotriazole unit to form a pentanuclear molecular unit. The pentanuclear nickel centres can be considered to be formed as a simple tetrahedral arrangement with four nickel species in four vertices of the tetrahedron

Table 1. Crystal data and structure refinement parameters for compound **I–III**.

Structural parameter	I	II	III
Empirical formula	C ₄₀ H ₂₄ N ₁₈ O ₄ Ni ₅	C ₇₈ H ₄₈ N ₃₆ O ₆ Ni ₉	C ₈₄ H ₆₀ N ₃₈ O ₈ Ni ₉
Crystal system	Trigonal	Triclinic	Triclinic
Space group	<i>P</i> - <i>3m1</i> (no.164)	<i>P</i> - <i>1</i> (no. 2)	<i>P</i> - <i>1</i> (no. 2)
<i>a</i> (Å)	15.5655(4)	11.3287(4)	12.2333(8)
<i>b</i> (Å)	15.5655(4)	14.0255(7)	12.3194(8)
<i>c</i> (Å)	10.0853(2)	15.5858(8)	16.9427(11)
α (°)	90.00	67.478(5)	78.068(5)
β (°)	90.00	74.944(4)	81.242(5)
γ (°)	120.00	68.186(4)	61.265(7)
<i>V</i> (Å ³)	2116.15(12)	2103.76(17)	2186.4(2)
<i>Z</i>	7	1	1
T/K	120(2)	120(2)	120(2)
ρ (calc/gcm ⁻³)	1.749	1.669	1.715
μ (mm ⁻¹)	2.250	2.042	1.973
λ (MoK α /Å)	0.71073	0.71073	0.71073
θ range (°)	2.52 to 30.39	2.50 to 26.00	2.46 to 26.00
Rint	0.0719	0.0318	0.0582
R indexes [<i>I</i> > 2 σ (<i>I</i>)]	R ₁ = 0.045; wR ₂ = 0.095	R ₁ = 0.043; wR ₂ = 0.100	R ₁ = 0.070; wR ₂ = 0.150
R indexes (all data)	R ₁ = 0.060; wR ₂ = 0.100	R ₁ = 0.056; wR ₂ = 0.107	R ₁ = 0.104; wR ₂ = 0.167

$R_1 = \sum |Fo| - |Fc| / \sum |Fo|$; $wR_2 = \{\sum [w(Fo^2 - Fc^2)] / \sum [w(Fo^2)]\}^{1/2}$. $w = 1/[\rho^2(Fo)^2 + (aP)^2 + bP]$. $P = [\max(Fo, O) + 2(Fc)^{-2}] / 3$ where $a = 0.0334$ and $b = 3.7387$ for **I**, $a = 0.0443$ and $b = 1.9999$ for **II**, $a = 0.0618$ and $b = 5.1530$ for **III**.

and the fifth nickel being present inside the tetrahedron. The different nickel centres are connected through six μ_3 -bta ligands. The octahedral nickel [Ni(1)], at the centre of the tetrahedron bonds through the nitrogen atoms of six different bta ligands. The tetrahedral nickel centres, occupying the vertices of the tetrahedron bonds through three nitrogen atoms of three different bta ligands. The fourth connection, needed for the tetrahedral coordination, is through the carbon of the [C = O]⁻ moiety, which is terminal. The packing view of the molecular pentamer units are shown in figure 2. As can be seen, the molecular units pack around the three fold symmetry axis. The terminal C = O units along with the benzene units from the benzene triazole moieties points towards the centre of the cavity. The molecular pentanuclear units are stabilised through extensive $\pi \dots \pi$ interactions between the benzene and triazole rings. The average distance between the benzene rings was 3.868 Å, suggesting reasonable $\pi \dots \pi$ interactions. CH – π interactions between the benzene rings from neighbouring clusters, found at a distance of 3.100 Å, could also contribute to the stability of the molecular pentamer units (figure S10).

3.2 Structure of [Ni₉(C₆H₄N₃)₁₂(CO)₆]**II** and [Ni₉(C₆H₄N₃)₁₂(CO)₆].2(C₃H₇NO)**III**

Compounds **II** and **III** have the same molecular cluster units composed of nine nickel centres. In compound **III**,

in addition to the nonameric cluster, two molecule of dimethyl formamide is also present. For crystal structure description, the structure of compound **II** would be presented here.

Compound **II** contains 65 non-hydrogen atoms in its asymmetric unit that comprises five crystallographically independent nickel atoms, six bta ligands, and three [C = O]⁻ moieties (figure S11). Of the five nickel atoms, one [Ni(1)] occupies a special position (*Ia*) with a site multiplicity of 0.5. Three nickel atoms, [Ni(3), Ni(4), Ni(5)] have distorted tetrahedral and the other two nickel atoms, [Ni(1), Ni(2)] have distorted octahedral geometry. Similar to the structure of **I**, all the tetrahedral nickel centres are bonded with three nitrogen atoms of the benzotriazole ligand and one carbon atom belonging to the terminal [C = O]⁻ moiety and the octahedral nickel centres are coordinated with six nitrogen atoms of the benzotriazole ligand (figure 3). The Ni-N bond distances are in the range of 1.969(3) – 2.110(3) Å and the Ni-C bond distances are in the range 1.628(11) – 1.635(3) Å, respectively. The average distances between the tetrahedral nickel centres was found to be 5.939 Å, the distance between the octahedral nickel centres was 3.702 Å and the distance between octahedral and tetrahedral Ni²⁺ atoms was 3.635 Å.

The arrangement of the nickel centres in **II** can be considered to be composed of two tetrahedral units joined through one of the vertices. This would lead to six free vertices, which are occupied by the tetrahedral

Table 2. Selected observed bond distances in the compounds **I–III**.

Bond	Distance (Å)	Bond	Distance (Å)
Compound I			
Ni(1)- N(2)	2.077(3)	Ni(2)-N(1)#1	2.005(3)
Ni(1)- N(2)#1	2.077(3)	Ni(2)-N(1)#2	2.005(3)
Ni(1)- N(2)#2	2.077(3)	Ni(2)- C(10)	1.650(6)
Ni(1)- N(5)	2.114(3)	Ni(3)- N(3)	1.993(3)
Ni(1)- N(5)#1	2.114(3)	Ni(3)- N(4)	1.985(2)
Ni(1)- N(5)#2	2.114(3)	Ni(3)- N(4)#3	1.985(2)
Ni(2)-N(1)	2.005(3)	Ni(3)- C(11)	1.637(4)
Compound II			
Ni(1)-N(1)	2.098(3)	Ni(3)-N(6)	2.001(3)
Ni(1)-N(1)#1	2.098(3)	Ni(3)-N(7)	2.003(3)
Ni(1)-N(9)	2.094(3)	Ni(3)-N(16)	1.990(3)
Ni(1)-N(9)#1	2.094(3)	Ni(3)-C(38)	1.635(3)
Ni(1)-N(12)	2.081(3)	Ni(4)-N(3)	1.990(3)
Ni(1)-N(12)#1	2.081(3)	Ni(4)-N(4)	1.994(3)
Ni(2)-N(2)	2.105(3)	Ni(4)-N(15)	1.983(3)
Ni(2)-N(5)	2.099(3)	Ni(4)-C(37)	1.635(3)
Ni(2)-N(8)	2.093(3)	Ni(5)-N(10)	1.980(3)
Ni(2)-N(11)	2.100(3)	Ni(5)-N(13)	1.969(3)
Ni(2)- N(14)	2.110(3)	Ni(5)-N(18)	1.991(3)
Ni(2)-N(17)	2.103(3)	Ni(5)-C(39)	1.628(4)
Compound III			
Ni(1)-N(1)	2.092(5)	Ni(3)-N(6)	1.983(5)
Ni(1)-N(1)#1	2.092(5)	Ni(3)-N(7)	1.986(5)
Ni(1)-N(12)	2.084(5)	Ni(3)-N(16)	1.995(5)
Ni(1)-N(12)#1	2.084(5)	Ni(3)-C(37)	1.636(6)
Ni(1)-N(18)	2.106(5)	Ni(4)-N(9)	1.992(6)
Ni(1)-N(18)#1	2.106(5)	Ni(4)-N(10)	1.998(5)
Ni(2)-N(2)	2.093(5)	Ni(4)-N(13)	1.995(5)
Ni(2)-N(5)	2.114(5)	Ni(4)-C(38)	1.625(6)
Ni(2)-N(8)	2.123(5)	Ni(5)-N(3)	1.990(5)
Ni(2)-N(11)	2.096(5)	Ni(5)-N(4)	1.997(5)
Ni(2)-N(14)	2.106(5)	Ni(5)-N(15)	1.996(5)
Ni(2)-N(17)	2.104(5)	Ni(5)-C(39)	1.618(6)

Symmetry transformations used to generate equivalent atoms: For **I**: #1 – $x + y, -x + 1, z$; #2 – $-y + 1, x - y + 1, z$; #3 – $-y + 1, -x + 1, z$; For **II**: #1 – $x + 2, -y + 2, -z$; For **III**: #1 – $x + 2, -y, -z$.

Ni. The central point where the two tetrahedron meet is also an octahedral nickel. Thus, there are three octahedral and six tetrahedral centres in this structure. The octahedral nickel centre [Ni(2)], occupying the centre of each tetrahedron bonds with six nitrogen atoms from six different bta ligands whereas the octahedral nickel centre [Ni(1)], at the meeting point of the two tetrahedra are bonded with nitrogen atoms from three bta ligands. All the tetrahedral nickel centres are connected with three nitrogen atoms from three different bta ligands and one terminal [C = O][−] moiety. The nonamer units pack in such a way to maximise the $\pi \dots \pi$ interactions between the benzene rings (figure 4). As can be seen from the figure 4, the packing of the nonamer units in **II** and **III** are different even though both the compounds crystallize in the same space group of *P-1*. This

is to accommodate the DMF solvent molecules in **III** within the structure. Thus, **II** and **III** may be considered as solvatomorphs. The nonanuclear units are stabilised through extensive $\pi \dots \pi$ interaction between the benzene rings (figure S12). The distance between the centre of benzene rings was 3.655 Å. In addition, CH – π interactions involving the benzene rings and triazole rings of neighbouring units at a distance of 3.257 Å would also contribute to the structural stability.

3.3 Structural comparison

Three molecular compounds Ni₅(C₆H₄N₃)₆(CO)₄, (**I**), [Ni₉(C₆H₄N₃)₁₂(CO)₆] (**II**) and [Ni₉(C₆H₄N₃)₁₂(CO)₆].2(C₃H₇NO) (**III**) containing five (**I**) and nine nickel (**II** and **III**) centres have been prepared and their structures

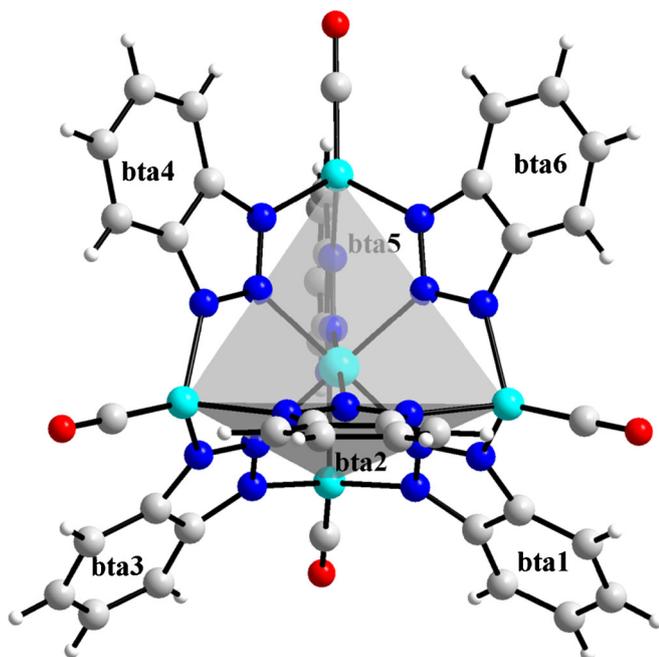


Figure 1. View of the pentamer cluster unit in **I**. The tetrahedral arrangement is highlighted (See text).

determined. As can be noted from the synthesis conditions, the three compounds were isolated employing the same synthesis mixture, but by a subtle variation of the reaction temperature. Of the three compounds, only **II** could be prepared in a pure single phasic form. Compound **I** appears as the major phase at lower temperature (150°C) whereas compound **III** appears only as a very minor phase. It is clear that there is a dynamic

equilibrium between the three phases during the synthesis. Heating the reaction mixture, either for longer duration or at higher temperature (180°C), results in a pure phase of **II**. In all the compounds, we observed that the terminal tetrahedral nickel centre is bonded to carbonyl moieties, which would have resulted due to the decomposition of the DMF solvent molecules under the reaction conditions. Similar observations have been made earlier.¹⁴ The penta and nona nuclear metal cluster compounds have been known earlier, but to the best of our knowledge this is the first report of a homo nuclear transition metal cluster compound containing the same metal (nickel) existing in both octahedral as well as tetrahedral coordinations.

The pentamer unit observed in **I** has also been described employing the Kuratowski graphic set rules.¹⁵ Accordingly, two different kinds of non-planar graphical representations, K5 and K3,3, can be considered. Of these, the latter can be defined as a complete bipartite graph of six vertices, three of which connect to each of the other three (figure S13). Compounds having this type of bonding have been described as Kuratowski type structures.^{15b} In table 3, we have listed the various compounds that have similar pentamer molecular structures. As can be noted, the central metal atom always has octahedral coordination and the terminal metals take different coordinations. Many of the structures were stabilised by weak interactions such as CH – π , π . . . π and hydrogen bonds.

Though compounds **II** and **III** are related to **I**, it is difficult to visualise the structure based on simple graphical notations of Kuratowski. We can describe the

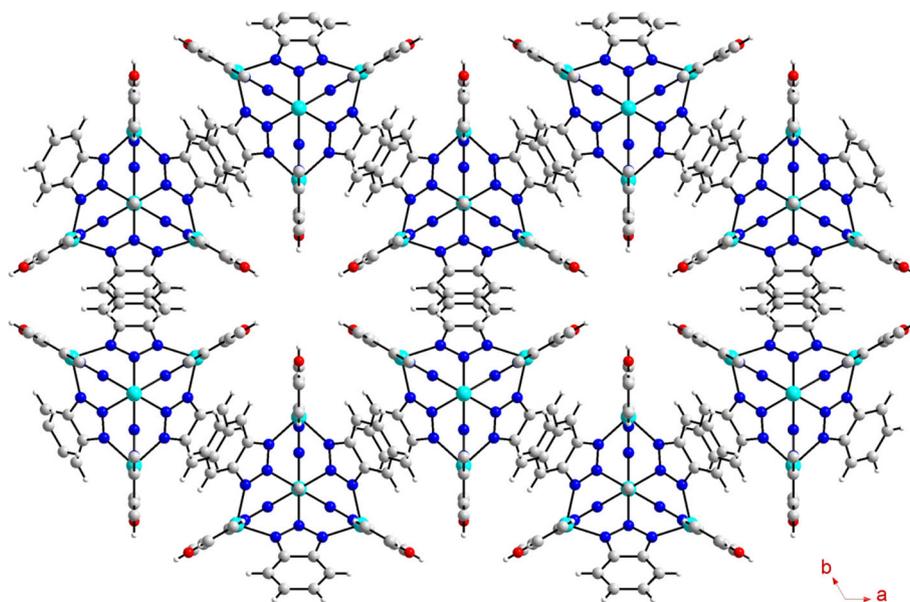


Figure 2. The packing view of the structure of **I** in the *ab* plane. Note the projection of the benzene rings towards the centre of the cavity.

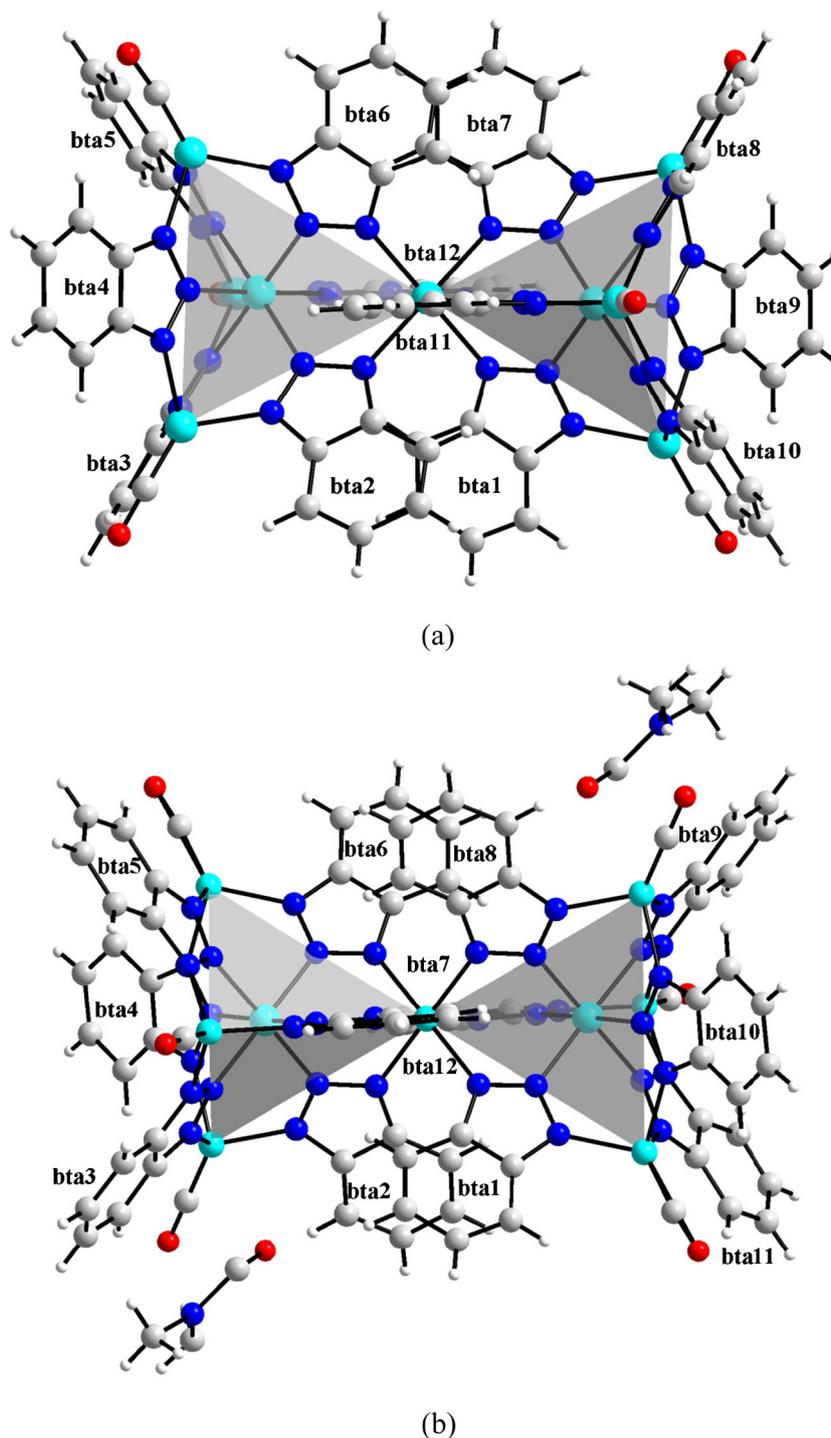


Figure 3. View of the nonamer cluster unit in (a) **II** and (b) **III**. The tetrahedral arrangement is highlighted.

nonanuclear structure as composed of two tetrahedral units joined through the vertex. This structure of the nonanuclear units resembles the $[P_2O_7]^{2-}$ structure. The compound, $[Zn_9Cl_6(OMe_2bta)_{12}] \cdot DMF$,³⁰ appears to closely resemble the structure of **II** and **III**. Compared to the pentamer compounds, the number of known nonamer phases is small (table 4).

The role of weak interactions in the stability of molecular complexes and low-dimensional structures have been discussed before.¹⁶ Presently, we have observed both $\pi \dots \pi$ as well as $CH - \pi$ interactions in all the three compounds. To evaluate the nature and strength of the weak interactions, theoretical calculations have been carried out. We have optimized these

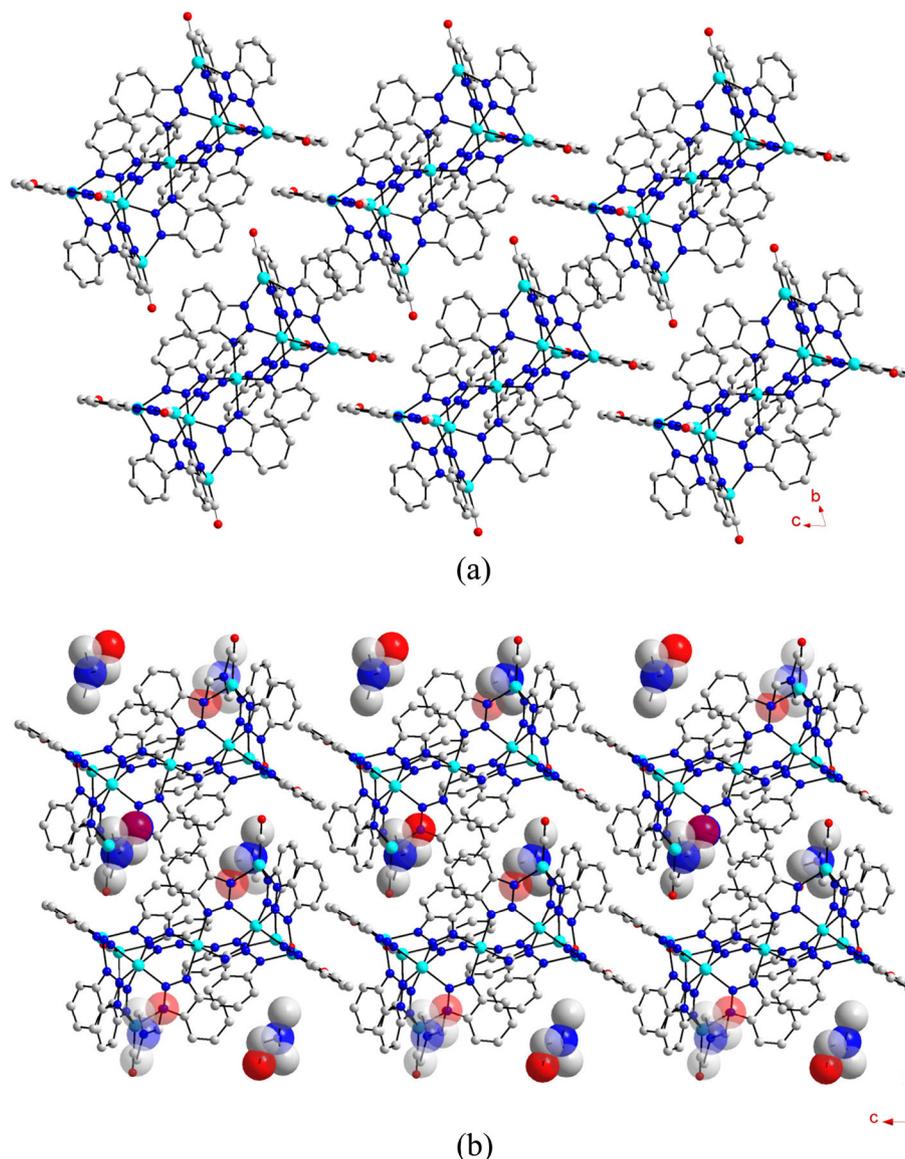


Figure 4. Packing view of the structures in the bc plane (a) **II** and (b) **III**.

compounds at M06-2X/6-31+G** level of theory¹⁷ using Gaussian-09 package.¹⁸ We have measured, the centroid–centroid distances (d) and inter-planar angle (θ) between the participating benzene and triazole moieties (figure 5). In all the compounds, the benzene rings were found to be aligned well with one over the other resulting in a inter-planar angles of 0° ($\theta = 0$). Looking at the arrangement of the benzotriazole units, we observed that the moieties have anti-parallel arrangement. From the quantum chemical calculations, independent benzotriazole units were expected to exhibit a dipole moment of 4.2 Debye. The perfect planarity of the benzotriazole units along with the anti-parallel arrangement results in the complete cancellation of the dipole moments of the bta in all the three compounds. Similar cancellation of the dipole moment

values involving phenanthroline units have been observed before.¹⁹ The lack of dipole moment gives rise to the π electron polarization resulting in favourable $\pi \dots \pi$ interactions. The DFT calculations on the three compounds reveal $\pi \dots \pi$ interaction energies of -9.04 , -6.83 and -6.84 kcal/mol, for **I**, **II** and **III**, respectively. These energies are lower than the estimated intermediate hydrogen bond strengths (approx. 10–15 kcal/mol) observed in the systems exhibiting N–H \dots O and O–H \dots O interactions.

From the DFT calculations, it appears that the strength of the weak interactions in **I** is more compared to **II** and **III**. The near equal values for the $\pi \dots \pi$ interaction energies in **II** and **III** indicates that the role of solvent molecules (DMF) is limited. It may be noted that we have not observed any hydrogen bond

Table 3. Summary of the known pentanuclear clusters.

S. No	Formula	Description	Ref
1	$[\text{Ni}_5(\text{bta})_6(\text{CO})_4]$	Octahedral Ni(II) atom surrounded by four tetrahedral Ni(II), bonded through six $\mu_{3-} \text{bta}^-$ ligands. The peripheral tetrahedral Ni(II) atoms have terminal C=O moiety.	This work
2	$[\text{Zn}_5(\text{acac})_4(\text{bta})_6] \cdot 4\text{C}_6\text{H}_{12}$	Octahedral Zn(II) atom is bonded with four penta coordinated metal centers through six $\mu_{3-} \text{bta}^-$ ligands. The peripheral penta coordinated Zn(II) are bonded with chelating <i>acac</i> .	29a
3	$[\text{Zn}_5(\text{bta})_6(\text{acac})_4(\text{DMF})]$. DMF $[\text{Zn}_5(\text{bta})_6(\text{acac})_4(\text{DMF})] \cdot 3.7\text{DMF}$	The octahedral central Zn(II) atom is connected with one octahedral and three square pyramidal Zn(II) atom through six $\mu_{3-} \text{bta}^-$ ligands. The square pyramidal Zn(II) atoms are bonded with <i>acac</i> ligand and the octahedral Zn(II) have both <i>acac</i> and DMF molecule.	29b
4	$[\text{Zn}_5(\text{bta})_6(\text{NO}_3)_4(\text{H}_2\text{O})]$	Octahedral Zn(II) atom is bonded with four penta coordinated zinc atoms through six $\mu_{3-} \text{bta}^-$ ligands. The penta coordinated zinc centers have terminal NO_3^- ions.	29c
5	$[\text{Zn}_5(\text{bta})_6(\text{NO}_3)_4(\text{H}_2\text{O})]$	The octahedral central Zn(II) atom is connected with one octahedral and three square pyramidal Zn(II) atom through six $\mu_{3-} \text{bta}^-$ ligands. The square pyramidal Zn(II) atoms are bonded with NO_3^- ions and the octahedral Zn(II) have both NO_3^- and H_2O molecule.	29d
6	$[\text{M}_5(\text{bta})_6(\text{NO}_3)_4(\text{H}_2\text{O})_4]$ (M=Co, Ni)	All the metal centers are octahedral with central one connected to others through 6 $\mu_{3-} \text{bta}^-$ ligands. The terminal metal centers are bonded by terminal NO_3^- ions and one H_2O molecule.	29e
7	$[\text{Ni}_5(5\text{Mebta})_6(\text{dbm})_4(\text{Me}_2\text{CO})_4]$	All the metal centers are octahedral with central one connected to others through 6 $\mu_{3-} 5\text{Mebta}^-$ ligands. The terminal metal centers are bonded by terminal <i>dbm</i> moiety and one Me_2CO molecule.	22
8	$[\text{Ni}_5(\text{OH})(\text{bta})_5(\text{acac})_4(\text{H}_2\text{O})_4]$ $[\text{Ni}_5(\text{OH})(5, 6\text{Me}_2\text{bta})_5(\text{acac})_4(\text{H}_2\text{O})_4]$	The octahedral Ni(II) are bridged through 5 $\mu_{3-} \text{bta}^-$ ligands and one $\mu_3 - \text{OH}^-$ ligand. Peripheral octahedral nickel centers are bonded by one chelating <i>acac</i> and H_2O molecule.	29f
9	$\text{Cu}_5\text{Cl}(\text{bta})_5(\text{PPh}_3)_4$ (a) and $\text{Cu}_5(\text{bta})_6(\text{RNC})_4$ (b)	The Cu centers exhibit both +1 and +2 oxidation states. The tetrahedral Cu(I) ions occupy the peripheral positions and the J-T distorted square pyramidal (a) and octahedral (b) Cu(II) occupy the middle. The Cu(I) centers are bonded with terminal PPh_3 and RNC molecules respectively.	29g and 29h

Table 3. (continued)

S. No	Formula	Description	Ref
10	[Zn ₅ Cl ₄ (Me ₂ bta) ₆]·2DMF [Co ^{II} Zn ₄ Cl ₄ (Me ₂ bta) ₆]·2DMF	Octahedral M [M = Zn(II) and Co(II)] atoms are bonded to tetrahedral Zn(II) atoms through by 6 μ_3 - Me ₂ bta ⁻ ligands. The peripheral tetrahedral Zn(II) are bonded by terminal Cl ⁻ ions.	29a
11	[MZn ₄ Cl ₄ (Me ₂ bta) ₆].2DMF (M ^{II} = Zn, Fe, Co and Cu) and [MZn ₄ Cl ₄ (Me ₂ bta) ₆].2C ₆ H ₅ Br (M ^{II} = Co, Ni)	The octahedral central metal atoms are connected with four tetrahedral Zn(II) metal atoms through six μ_3 - Me ₂ bta ⁻ ligands. The peripheral tetrahedral Zn(II) atoms are bonded with terminal Cl ⁻ ions.	15
12	[Ru ^{II} Zn ₄ Cl ₄ (Me ₂ bta) ₆]·2DMF	Octahedral Ru(II) atom is connected with four tetrahedral Zn(II) atoms through μ_3 - Me ₂ bta ⁻ ligands. The peripheral tetrahedral Zn(II) atoms are bonded with terminal Cl ⁻ ions.	29i
13	[Zn ₅ (Me ₂ - bta) ₆ Cl ₄ (H ₂ O) ₂]	Octahedral Zn(II) atom is bonded with four tetrahedral Zn(II) atoms through six μ_3 - Me ₂ bta ⁻ ligands. The tetrahedral Zn(II) atoms have terminal Cl ⁻ ions.	29c
14	[Zn ₅ Cl ₄ (ta) ₆]	Octahedral Zn(II) atom is bonded with four tetrahedral Zn(II) atoms through six μ_3 - ta ⁻ ligands. The peripheral tetrahedral Zn(II) atoms have terminal Cl ⁻ ions.	29i

bta = 1,2,3- benzotriazole; ta = 1,2,3-triazole; Me₂bta - 5,6-dimethyl-1,2,3-benzotriazole; 5Mebta - 5-methyl-1,2,3-benzotriazole; DMF = *N, N'*- dimethyl formamide; PPh₃ = Triphenylphosphine, acac = acetylacetonate; dbm - dibenzoylmethane. Me₂CO - acetone.

interaction between the solvent molecules and the nonamer clusters in **III**, suggesting that the $\pi \dots \pi$ interaction are the dominant stabilization force in **II** and **III**. The higher stabilization energy observed in **I** could be due to the favourable arrangement of the *bta* ligands, which are arranged around the 3-fold symmetry axis.

Though we have been able to make a reasonable estimate of the weak interactions responsible for the stability of the molecular complexes **I**, **II** and **III**, the selective formation of one of the species (**II**) at higher temperature prompted us to investigate the possible transformation reactions.

3.4 Structural transformation studies

A close examination of the oxoclusters in the present compounds suggested that they may be related. Theoretically, two pentamer clusters can give rise to the nonamer cluster by careful merging. In such a scenario, the two terminal nickel centres could merge to form the dimer similar to the formation of [P₂O₇] dimers from two [PO₄] units. The resulting nickel centre in the

present compounds (**II** and **III**) becomes octahedral. A schematic of such a transformation is given in scheme 1. If this assumption is true, then, it may also be possible to transform the pentameric cluster unit into nonameric clusters. It may be noted that the formation of both the pentamer (**I**) as well as the nonamer clusters (**II** and **III**) was effected at 150°C. In order to test this hypothesis, two sets of experiments were carried out. In one set of studies, the reaction mixture was allowed to react at 150°C for a period of 7 days and in the other case, the mixture of phases isolated by reacting the original mixture at 150°C for 3 days was filtered, dried and then employed as the starting source. In a separate experiment, we have reacted the single crystals of compound **I** at 180°C for 3 days. The products of the reaction were investigated by PXRD (figure S14–S16). The purpose of this exercise is to investigate the most stable phase in the reaction between the nickel salt and the benzotriazole at 150°C and 180°C as a function of time. In all the cases, we observed the formation of pure phase of **II**. It may be noted that compound **III** appears only as a minor phase

Table 4. Summary of the known nonanuclear clusters.

S. No	Formula	Description	Ref
1	[Ni ₉ (bta) ₁₂ (CO) ₆] [Ni ₉ (bta) ₁₂ (CO) ₆].2DMF	Three octahedral Ni(II) atoms are bonded with six other tetrahedral nickel atoms through 12 μ_3 -bta ⁻ ligands. The peripheral tetrahedral nickel centers are coordinated with C = O ⁻ ions.	This work
2	[Ni ₉ (bta) ₁₂ (NO ₃) ₆ (MeOH) ₆].4THF [Co ₉ (bta) ₁₂ (MeOH) ₁₈][(NO ₃) ₆].9C ₆ H ₆	The octahedral metal centers M [M = Ni(II) and Co(II)] are bonded through 12 μ_3 -bta ⁻ ligands. The peripheral octahedral nickel centers are coordinated with one NO ₃ ⁻ ions and one MeOH molecule whereas the cobalt centers have terminal 3 MeOH molecule.	9
3	[Zn ₉ (bta) ₁₂ (acac) ₆].6DMF	Three octahedral Zn(II) atoms are bonded with six other distorted square pyramidal zinc atoms through 12 μ_3 -bta ⁻ ligands. The peripheral square pyramidal zinc centers are coordinated with one acac.	29b
4	[Ni ₉ (Me ₂ bta) ₁₂ (bzac) ₆ (MeOH) ₆]	The octahedral nickel centers are octahedral which are bonded through 12 μ_3 -Me ₂ bta ⁻ . The peripheral octahedral nickel centers are coordinated with one bzac ligand and one MeOH molecule.	22
5	[Zn ₉ (Me ₂ bta) ₁₂ (CH ₃ COO) ₆].3DMF	Three octahedral Zn(II) atoms are bonded with six other distorted square pyramidal zinc atoms through 12 μ_3 -Me ₂ bta ⁻ ligands. The peripheral square pyramidal zinc centers are bonded with terminal CH ₃ COO ⁻ ions.	9
6	[Zn ₉ Cl ₆ (OMe ₂ bta) ₁₂].DMF [Fe ₃ ^{II} Zn ₆ Cl ₆ (OMe ₂ bta) ₁₂].DMF	Three octahedral metal M [M = Zn(II) and Fe(II)] atoms are bonded with six other tetrahedral zinc atoms through 12 μ_3 -OMe ₂ bta ⁻ ligands. The peripheral tetrahedral zinc centers are coordinated with Cl ⁻ ions.	30

bta = 1,2,3- benzotriazole; Me₂bta - 5,6-dimethyl-1,2,3-benzotriazole; OMe₂bta - 5,6-dimethoxy-1,2,3-benzotriazole DMF = N, N'- dimethyl formamide; bzac – benzoylacetone.

in the reaction and it is not surprising that the solvent molecule, DMF, can be removed easily from the structure of **III** forming **II**. The studies on the transformation of **I** to **II**, carried out at 180°C, does not suggest the formation of **III**. This may indicate that **III** could be a transient intermediate formed at lower temperatures. Such observation have been made earlier during the transformation studies of phosphates.²⁰ In all the transformation reactions, **II** appears to be the only product at 150°C and 7 days as well as at the higher temperature (180°C/3 days). The studies also clearly suggest that the pentamer (**I**) is reactive and transforms to **II** at elevated temperatures. Studies of this nature are necessary for our understanding of the formation of related phases under reaction conditions and help to fine tune

the synthetic conditions for the preparation of newer compounds.

3.5 Optical studies

Room temperature UV-Vis spectroscopic studies on **II** and bta ligand exhibited four distinct transitions at 260, 325, 390, 585 nm for (**II**) and two at 260, and 302 nm for the bta ligand (figure S4 and S5). The two peaks at 260 and 325 nm, could be due to the $\pi - \pi^*$ and $n - \pi^*$ intraligand transitions and the transitions of the benzotriazole ligands, respectively. The transitions at ~ 390 and 585 nm, are due to the spin allowed transition from ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ transitions of the octahedral Ni(II) atom.^{15b} The other possible

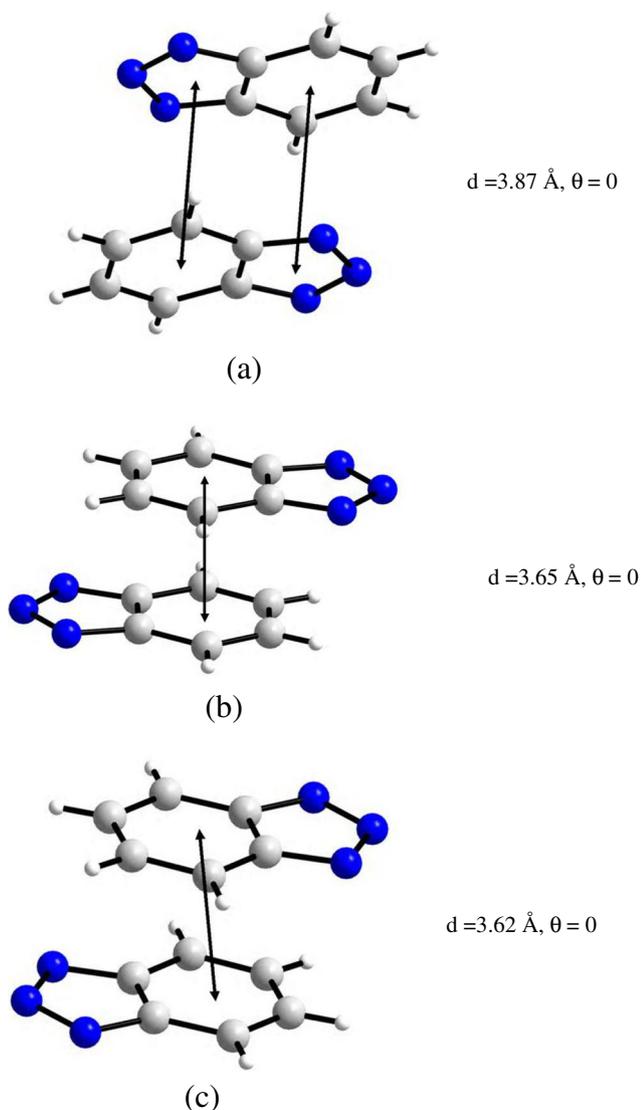


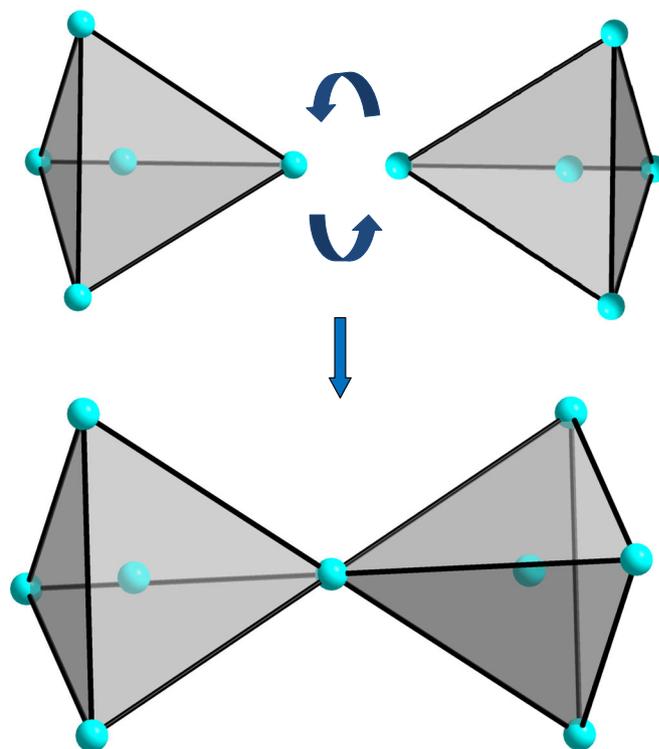
Figure 5. View of the arrangement of the benzotriazole units (a) **I**, (b) **II** and (c) **III**.

transitions like ${}^3T_1(F) \rightarrow {}^3T_1(P)$ and ${}^3T_1(F) \rightarrow {}^3T_2(F)$ from tetrahedral nickel centres probably overlaps with the observed transitions of the octahedral Ni.

The photoluminescence spectra for compound **II** and benzotriazole ligand were studied using an excitation wavelength of 260 nm. Emission bands for compound **II** and benzotriazole ligand are observed at 397 nm and 392 nm respectively (figure S6). These emission bands could be due to the intraligand transitions.²¹ Emission bands of compound **II** are red shifted compared to the benzotriazole ligand.

3.6 Magnetic studies

The dc magnetic susceptibility measurement for **II** was carried out in the temperature range 2–300 K in an



Scheme 1. Transformation of pentamer to nonamer.

applied magnetic field of 1000 Oe. The molar magnetic susceptibility (χ_m) was found to be $0.04 \text{ emu mol}^{-1}$ at room temperature, which did not exhibit any appreciable change upto 50K. The χ_m value increases sharply upon cooling further and reaches a value of 0.3 emu mol^{-1} at 2 (figure 6a). The thermal dependence of $1/\chi_m$ is shown as an inset in figure 6a. The effective magnetic moment (μ_{eff}) of **II** decreases from $1.13 \mu_B$ per Ni^{2+} ions (at 298 K) to a value of $0.30 \mu_B$ at 2K (figure 6b). This suggests net antiferromagnetic interactions in this temperature range. We did not observe any abrupt increase in the μ_{eff} values upto the lowest temperatures, which suggests that the nonamer nickel units do not have any long-range ferromagnetic correlations. It is likely that the tetrahedral nickel species which surrounded the octahedral core nickel in this structure do not contribute magnetically. The possibility of the tetrahedral Ni^{II} ions in the low spin state ($d^8 = t_{2g}^6; e_g^2$), is also supported by the UV-Vis spectroscopic studies (figure S5). We did not observe any transitions corresponding to the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ and ${}^3T_1(F) \rightarrow {}^3T_2(F)$ of the tetrahedral nickel. Similar magnetic behaviour has been observed earlier.^{9,22} The magnetic data was fitted for the Curie-Weiss behaviour, in the temperature range 200–300K (figure 6a inset). From the fit, the values of Curie constant and Weiss constant was found to be $C = 26.9 \text{ emu K mol}^{-1}$ and $\theta_p = -36.4 \text{ K}$

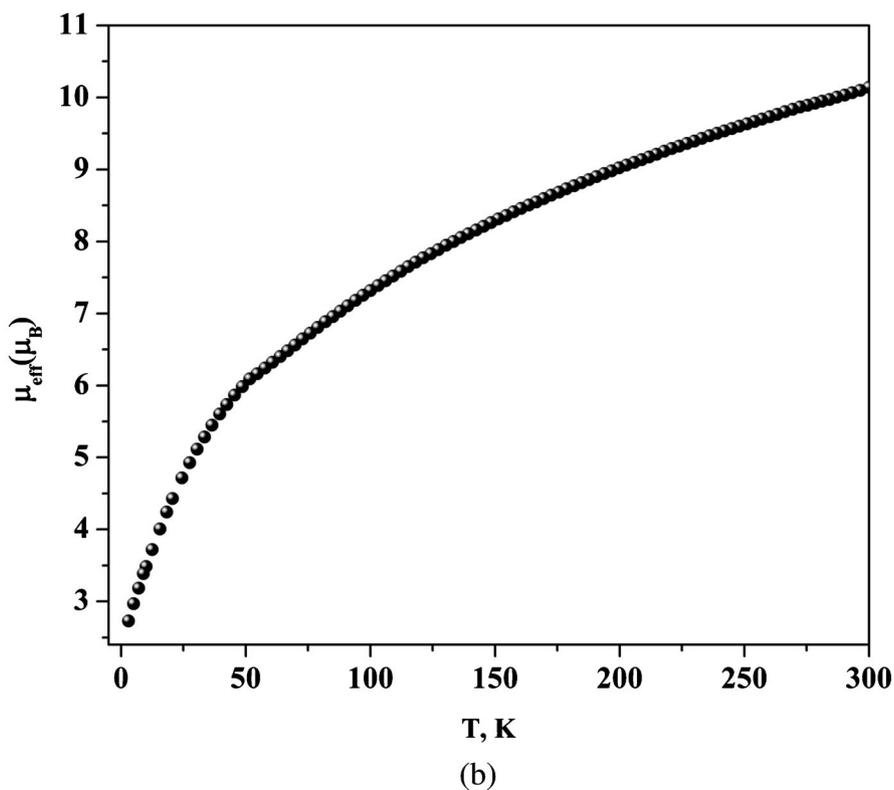
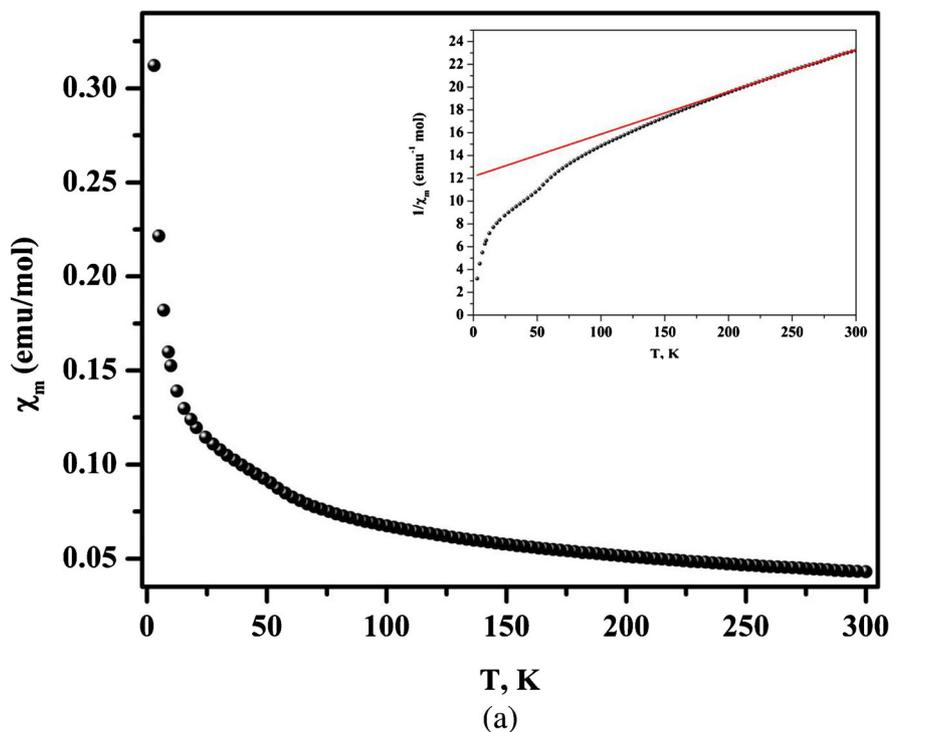


Figure 6. (a) The thermal variation of the magnetic susceptibility of **II**. Inset shows the $1/\chi_m$ vs. T plot. (b) The thermal variation of the effective moment (μ_{eff}) in **II**.

per Ni centre. The rather high negative value for the θ_p indicates the presence of strong antiferromagnetic interactions between the Ni^{2+} centres. Similar behaviour has been observed before.^{9,23}

3.7 Thermal decomposition studies

Our TGA studies indicated that the product of decomposition is NiO. We have previously employed thermal

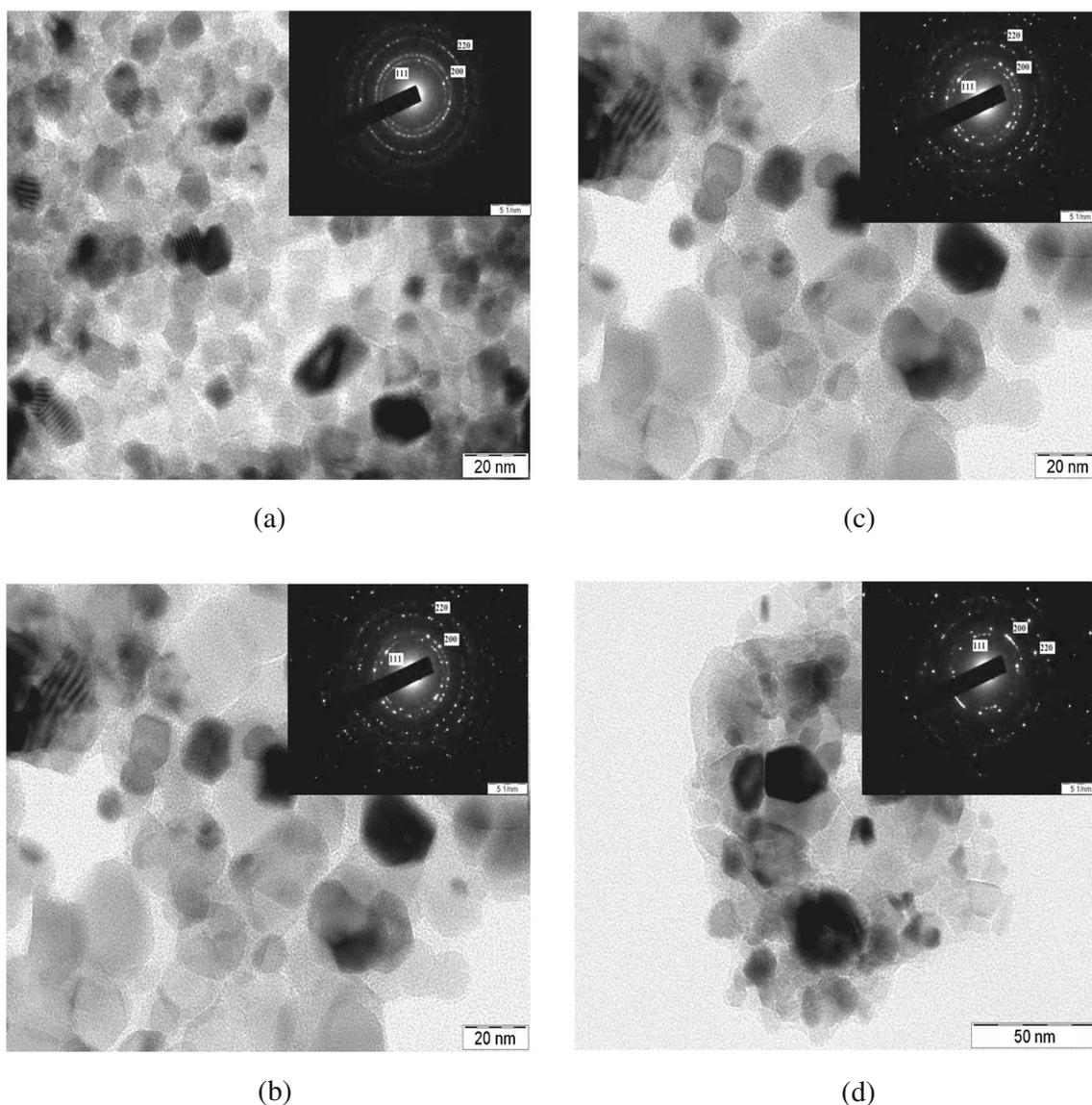


Figure 7. The transmission electron microscopic (TEM) images of the heated samples of **II**. Inset shows the SAED patterns. (a) 375°C, (b) 500°C, (c) 650°C, and (d) 850°C. All the samples show NiO phases predominantly (See text).

decomposition of mixed metal MOF compounds with extended structures as the precursor to prepare oxides such as GdCO_3 ,²⁴ CoMn_2O_4 ²⁵ and NiMn_2O_4 .²⁶ The temperature of decomposition hold importance on the morphology, particle size, catalytic reactivity, etc.^{24–26} We wanted to explore the decomposition of the nonamer (**II**) for preparing NiO phases of different morphologies and particle sizes. To this end, compound **II** was heated in a simple muffle furnace at 375, 500, 650, 850°C for 4 h under atmospheric conditions. The products were analysed using PXRD. From the PXRD studies, we observed that at lower temperatures (375, 500°C) both NiO as well as small amounts of metallic Ni were formed (figure S19). As the temperature is raised, NiO was the only product observed, which is

in confirmation to what was observed during the TGA studies. We have determined the average particle size of the NiO using the Debye-Scherrer formula.²⁷ The particle size, as expected, were low at lower temperatures and larger at higher temperature. The variation in the particle size of NiO was also confirmed independently by the TEM studies, which also agree with the observations of PXRD (figure 7). The variation of the particle size as a function of temperature was similar to those observed before (table S5).²⁸

4. Conclusion

The synthesis and structure of three closely related molecular nickel complexes, $[\text{Ni}_5(\text{bta})_6(\text{CO})_4]$, **I**, $[\text{Ni}_9$

(bta)₁₂(CO)₆], **II**, and [Ni₉(bta)₁₂(CO)₆]. 2(C₃H₇NO), **III**, have been accomplished. All the three compounds have been prepared using the same reaction composition. During the course of this study, we have been able to show that the pentamer (**I**) could be a reactive intermediate in the formation of the nonamer compounds (**II** and **III**). The compounds **II** and **III** can be considered as solvotamorphs. To the best of our knowledge, this is the first report of penta and nonanuclear complexes having the same transition element in two distinct coordination environments. Magnetic studies indicate that the nonamer compound, **II**, has strong antiferromagnetic behaviour. The present study reveals the richness of the metal oxo clusters, which appear to depend on the subtle relationships between the reaction composition and temperature. It is likely that many such compounds can be prepared by varying the synthetic conditions suitably. Efforts towards this goal are presently underway.

Supporting Information

Selected bond angles for the compounds **I–III** (table S1); Synthesis composition and conditions employed for the preparation of compounds **I–III** (table S2); Structures of table 3 (table S3); Structures of table 4 (table S4); Preparation conditions and textural characterization of compound **II** (table S5); Powder XRD patterns of the compound **I** (figure S1); Powder XRD patterns of the compound **II** (figure S2); IR spectra for the compounds **II** (figure S3); UV-Vis spectra of benzotriazole ligand (figure S4); UV-vis spectra of the compounds **II** (figure S5); Photoluminescence spectra of the ligand benzotriazole along with compound **II**, (figure S6); TGA of the compounds **II** (figure S7); Powder XRD (Cu $\kappa\alpha$) pattern of the compound **II** after TGA (figure S8); Asymmetric unit in compound **I** (figure S9); Figure shows various $\pi \dots \pi$ and CH – π interactions in compounds **I** (figure S10); Asymmetric unit for compound **III** has been changed (figure S11); Figure shows various $\pi \dots \pi$ and CH – π interactions in compounds **II** and **III** (figure S12); Derivation of K_{3,3} graphical representation from pentanuclear structure (figure S13); Powder XRD patterns of the transformation reaction from compound **I** to **II** through **III** (figure S14); Mixture of three phase ($2\theta = 5\text{--}20$), (figure S15a); Mixture of three phase ($2\theta = 6.8\text{--}20$), (figure S15b); Transformation of the mixed phase obtained at 150°C/72h to pure phase of **II** by heating at 180°C/72h (figure S16); Variation of $\chi_M T$ vs T plot as a function of applied dc field (figure S17); M vs H plot picture

corrected (figure S18); Powder XRD (Cu $\kappa\alpha$) pattern of the compound **II** heated at different temperature (375–850°C) (figure S19); Scheme S1: Transformation of compound **I** and **III** into compound **II**.

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