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Dinuclear and heptanuclear nickel(II) complexes: Anion coordination induced ligand arm hydrolysis and aggregation around a nickel(II) core

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ABSTRACT

The heptanuclear and tetracationic nickel(II) complex $[Ni_7(\mu_3-OH)_6(\mu_3-H_2L)_4](NO_3)_4$ ·2MeOH (**3**·2MeOH); (H₃L is 2,6-bis-[(3-hydroxy-propylimino)-methyl]-4-methyl-phenol), featuring four defective cubanes around a pivotal nickel(II) ion, has been obtained *via* hydroxido-bridge-induced assemblage of two Ni₃ fragments. Presence of azido (N₃⁻) and bromido (Br⁻) ions in reactions on the contrary lead to one ligand imine arm hydrolysis and formations of $[Ni_2(N_3)_2(\mu-HL1)_2(OH_2)_2]$ (**1**) and $[Ni_2Br_2(\mu-HL1)_2(OH_2)_2]$ (**2**); where H₂L1 is 2-hydroxy-3-[(3-hydroxy-propylimino)-methyl]-5-methyl-benzaldehyde. X-ray structural analyses of **3** show six symmetrically positioned Ni^{II} around a central Ni^{II} and bridged by six *in situ* generated hydroxido groups from solvent water molecules. Density functional theory (DFT) calculations have also been performed to predict magnetic behavior of the complexes. The spin density surface of compounds **1** and **2** has been also obtained.

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1. Introduction

During conventional room temperature solvent based synthesis of high-nuclearity transition metal complexes, as opposed to high temperature hydrothermal route, it is always very difficult to understand the exact course of reaction [1a-d]. The supramolecular aggregate process is largely dependent upon the solvent system, metal salts, temperature, concentrations of the reacting ingredients and pH. Thus the contributing factors that control the synthesis of high-nuclearity complexes are still not well recognized. There is a continuing need for newer synthetic methodologies to obtain such species. Synthetic access to nickel(II) based multinuclear aggregates showed renewed interests for their recently identified single-molecule magnet behavior and expected potential to serve as synthetic models for metallobiomolecules [2,3]. In the emerging area of cluster-based coordination systems, significant progress has been made in recent years in sorting out the formation and growth mechanism of 3d metal ion clusters. Quite often this category of compounds is typically synthesized via 'serendipitous self-assembly' processes by allowing ligand bound metal ions to condense around the appropriate bridging and/or nucleating ligands [4,5]. Several 'fused defective cubanes' within the giant structure is a common structural feature often

observed in transition metal coordination chemistry [6–15]. In these cubanes, the vertices are composed of either the metal ions or ligand donor atoms (μ - and μ ₃-O). The *in situ* generated or externally added hydroxido group is a very appropriate bridging ligand in the construction of this motif, and its relevance in cluster coordination chemistry has not studied much [16-18]. Polymetallic nickel compounds involving hydroxido ligands as principal bridges are still limited [2,17]. The existing hydroxido-based multinuclear nickel compounds comprising fused cubanes feature the nuclearities {Ni₆}, [27] {Ni₇}, [2] {Ni₆} [13] and {Ni₇} [17]. Use of phenoxide centered binucleating Schiff base ligands for the construction of trinuclear compounds has recently been achieved by us for a Zn₃ species [28]. Assembly of two such species around a core metal ion can give rise to a heptanuclear compound of new molecular structure and symmetry. Such ligands bearing imine groups are prone to hydrolysis in presence of different metal salts and other ancillary groups. In this context, we have focused our attention to explore the reactivity of Schiff base ligand H₃L (Chart 1, left) with two different nickel(II) salts and ancillary ligands. The aggregating ability of nickel(II) bound-H₃L, together with the in situ generated hydroxido groups, has now been exploited here with the preparation of a novel heptanuclear complex $[Ni_7(\mu_3-OH)_6(\mu_3-H_2L)_4](NO_3)_4$ ·2MeOH (3-2MeOH). Unlike of our previous report of a azido-bridged {Ni₆} complex, the presence of azido anions in the present synthesis gave only dinuclear compound $[Ni_2(N_3)_2(\mu-HL1)_2(OH_2)_2]$ (1). Bromide anions also provided a similar one as $[Ni_2Br_2(\mu-HL1)_2(OH_2)_2]$ (2). In the latter two cases, one of the non-coordinating dangling



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Scheme 1. Ni(II) coordination induced one-arm-hydrolysis of H₃L.



Scheme 2. Crystallographically established binding modes of H_1L1^- and H_2L^- in complexes 1–3.

ligand arm on each ligands undergoes hydrolysis in the presence of $Ni(NO_3)_2 \cdot 6H_2O$ and $NiBr_2 \cdot 3H_2O$ (Scheme 1). The hydrolyzed and unhydrolyzed H_3L have shown two types of binding behavior (Scheme 2).

The study reported in this paper on anion-bridge induced self-assembly provides new examples of ligand for the exclusive formation of dinuclear and heptanuclear complexes of nickel(II) depending on the reaction condition and *in situ* generation of bridging hydroxido groups.

2. Experimental section

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2.1. Materials and physical methods

The chemicals used were obtained from the following sources: nickel nitrate from S.D. Fine Chem (India), 3-amino-1-propanol from Aldrich Chemical Co. Inc. and triethylamine, sodium azide from Merck (India). 2,6-Diformyl-4-methylphenol (2-hydroxy-5methyl-benzene-1,3-dicarbaldehyde) was prepared following a literature procedure [29]. Nickel(II) bromide trihydrate (NiBr₂·3H₂O) was prepared by the treatment of basic nickel(II) carbonate, NiCO₃·2Ni(OH)₂·4H₂O (AR grade, E. Merck, India), with hydrobromic acid (AR grade, E. Merck, India), followed by slow evaporation on a steam bath. It was then filtered through a G4 glass frit and stored in a CaCl₂ desiccator. All other chemicals and solvents were reagent grade materials and were used as received without further purification. Elemental analyses (C H N) were performed with a Perkin–Elmer model 240C elemental analyzer. FT-IR spectra were recorded on a Perkin–Elmer 883 spectrometer. The solution electrical conductivity and electronic spectra were obtained using a Unitech type U131C digital conductivity meter with a solute concentration of about 10^{-3} M and a Shimadzu UV 3100 UV–Vis–NIR spectrophotometer, respectively.

2.2. Synthesis

2.2.1. 2,6-Bis-[(3-hydroxy-propylimino)-methyl]-4-methyl-phenol (H₃L)

To a MeOH solution (20 mL) of 2,6-diformyl-4-methylphenol (1.0 g, 6.1 mmol), 3-amino-1-propanol (0.91 g, 12.2 mmol) was added in air at room temperature (28 °C) and stirred for 2 h to give an orange colored semi-solid product after complete evaporation of solvent in air for 12 h. The semi-solid product 2,6-bis-[(3-hydro-xy-propylimino)-methyl]-4-methylphenol thus obtained was washed with water and used directly without further purification for complexation reactions. Yield: 1.32 g (78%).

2.2.1.1. $[Ni_2(N_3)_2(\mu - HL1)_2(OH_2)_2]$ (**1**). To the MeOH solution (20 mL) of H₃L (0.278 g, 1.00 mmol) a MeOH solution (10 mL) of Ni(NO₃)₂. 6H₂O (0.290 g, 1.0 mmol) was added slowly and stirred under aerobic conditions at room temperature. After half an hour, NaN₃ (0.65 g, 1.0 mmol) and then NEt₃ (0.139 mL, 0.101 g, 1.00 mmol) in methanol was added while stirring and the mixture was stirred for 2.5 h. The solvent was evaporated in air to give a green solid, which was isolated, washed with cold methanol and dried under vacuum over P₄O₁₀. Green crystals suitable for X-ray analysis were obtained from recrystallization of a MeOH solution of the above green solid after three weeks. Yield: .494 g, 73%. Anal. Calc. for C₂₄H₃₂Ni₂N₈O₈ (677.99 g mol⁻¹): C, 42.51; H, 4.75; N, 16.52. Found: C, 42.42; H, 4.63; N, 16.42%. Selected FT-IR bands: (KBr, cm⁻¹; s = strong, vs = very strong, m = medium, br = broad) 3401(b), 2926(m), 2345(m), 2099(vs), 1642(s), 1456(s), 1346(s), 1236(s), 1146(s), 1121(s), 1076(s), 1032(m), 771(s), 637(s), 504(m). Molar conductance, $\Lambda_{\rm M}$: (MeOH solution) 96.5 Ω^{-1} cm² mol⁻¹. UV–Vis spectra [λ_{max} , nm (ϵ , L mol⁻¹ cm⁻¹)]: (MeOH solution) 674 (401), 368 (8519), 260 (67094).

2.2.1.2. $[Ni_2(Br)_2(\mu-HL1)_2(OH_2)_2]$ (2). To the MeOH solution (20 mL) of H₃L (0.278 g, 1.00 mmol) a MeOH solution (10 mL) of NiBr₂·3H₂O (0.272 g, 1.0 mmol) was added slowly followed by NEt₃ (0.139 mL, 0.101 g, 1.00 mmol) and stirred for 3 h at room temperature. The solvent was evaporated in air to give a light green solid, which was isolated, washed with cold methanol and dried under vacuum over P₄O₁₀. Green crystals suitable for X-ray analysis were obtained from recrystallization of a MeOH solution of the above obtained light green solid after two weeks. Yield: .572 g, 76%. Anal. Calc. for C₂₄H₃₂Ni₂N₂O₈Br₂ (753.75 g mol⁻¹): C, 38.24; H, 4.27; N, 3.71. Found: C, 38.12; H, 4.23; N, 3.62%. Selected FT-IR bands: (KBr, cm^{-1} ; s = strong, vs = very strong, m = medium, br = broad) 3424(br), 1639(vs), 1458(vs), 1243(s), 1089(s), 972(s), 846(m), 764(s), 740(s), 698(s), 530 (s). Molar conductance, $\Lambda_{\rm M}$: (MeOH solution) $102 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. UV–Vis spectra [λ_{max} , nm (ε , L mol⁻¹ cm⁻¹)]: (MeOH solution) 663 (119), 372 (1199), 259 (96903).

2.2.1.3. $[Ni_7(\mu_3-OH)_6(\mu-H_2L)_4](NO_3)_4$ ·2MeOH (**3**·2MeOH). To the MeOH solution (20 mL) of H₃L (0.278 g, 1.00 mmol) a MeOH solution (10 mL) of Ni(NO_3)_2·6H₂O (0.580 g, 2.0 mmol) was added slowly followed by NEt₃ (0.139 mL, 0.101 g, 1.00 mmol) and stirred for 2.3 h at room temperature. The solvent was evaporated in air to give a green solid, which was isolated, washed with cold methanol and dried under vacuum over P₄O₁₀. Green plate-like crystals suitable for X-ray analysis were obtained from recrystallization of a

MeOH solution of the above isolated green solid after 18 days. Yield: 0.663 g, 68%. *Anal.* Calc. for $C_{62}H_{98}Ni_7N_{12}O_{32}$ (1934.49 g mol⁻¹): C, 38.50; H, 5.11; N, 8.69. Found: C, 38.42; H, 5.03; N, 8.52%. Selected FT-IR bands: (KBr, cm⁻¹; s = strong, vs = very strong, m = medium, br = broad) 3398(br), 2926(s), 1638(s), 1549(s), 1383(vs), 1235(s), 1239, 1058(vs), 970(m), 618(m). Molar conductance, A_{M} : (MeOH solution) 391.5 Ω^{-1} cm² mol⁻¹. UV–Vis spectra [λ_{max} , nm (ε , L mol⁻¹ cm⁻¹)]: (MeOH solution) 673 (417), 371 (1813), 260 (89459).

2.3. Theoretical methods

Calculations have been carried out using density functional theory (DFT) combined with the broken symmetry approach [19,20] by means of GAUSSIAN 09 package [21]. The level of theory used in this study is B3LYP/6-31+G* which is a good compromise between the size of the system and the computational demands. For these calculations we have used the crystallographic coordinates. It should be mentioned that the widely and successfully used [22-24] broken symmetry DFT approach is not the unique methodology to compute and interpret magnetic properties in quantum chemistry. For instance ab initio methods based on Difference Dedicated Configuration Interaction [25] (e.g. CASSCF/DDCI) give excellent results and offers the possibility to finely analyze the mechanisms and origin of magnetic properties taking advantage of the access to the wavefunction of all spin states of interest. This approach has been recently used in the study of cis/trans isomeric effects on magnetic properties of copper complexes [26].

2.4. X-ray crystallography

The diffraction data of the complex **1**, **2** and **3**-2MeOH was collected on a Bruker APEX-II CCD X-ray diffractometer using single crystals that uses graphite-monochromated Mo K α radiation (λ = 0.71073 Å) by ω -scan method at 293 K. Information concern-

Table 1

Crystal	lographic	data fo	r 1, 2	and	3 ·2MeOH.
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ing X-ray data collection and structure refinement of the compound is summarized in Table 1. For complex **1** a total of 4445 reflections were recorded with Miller indices $h_{\min} = -12$, $h_{\max} = 12$, $k_{\min} = -22$, $k_{\max} = 19$, $l_{\min} = -17$, $l_{\max} = 15$. For complex **2** a total of 4220 reflections were recorded with Miller indices $h_{\min} = -12$, $h_{\max} = 12$, $k_{\min} = -21$, $k_{\max} = 21$, $l_{\min} = -15$, $l_{\max} = 16$. For **3** 2MeOH, a total of 6680 reflections were recorded with Miller indices $h_{\min} = -28$, $h_{\max} = 28$, $k_{\min} = -22$, $k_{\max} = 22$, $l_{\min} = -17$, $l_{\max} = 16$. In the final cycles of full-matrix least squares on F^2 , all non-hydrogen atoms were assigned anisotropically. The structures were solved using the shelx-97 [30] program system. For the structure **3**-2MeOH the probable presence of other solvent molecules was treated, during the refinement, by means of the routine squeeze included in the PLATON system of programs [31].

3. Results and discussion

3.1. Synthetic considerations

The Schiff base ligand 2,6-bis-[(3-hydroxy-propylimino)methyl]-4-methyl-phenol (H₃L) was prepared (Scheme S1 in the Supporting Information) following a modified literature procedure [28]. The first two complexes of this series to be identified were the green binuclear ones $[Ni_2(N_3)_2(\mu-HL1)_2(OH_2)_2]$ (1) and $[Ni_2Br_2]$ $(\mu$ -HL1)₂ $(OH_2)_2$ (**2**), obtained from the reactions of Ni(NO₃)₂·6H₂O plus NaN₃ and NiBr₂·3H₂O in NEt₃ added methanolic H₃L in 73% and 76% yields. Room temperature stirring was done for 2.5 and 3 h using a 1:1 ligand to metal salt stoichiometry for **1** and **2**. respectively. The synthesis of **1** and **2** are summarized by Eqs. (1) and (2), considering the coordination induced hydrolytic transformation of H_2L^- to $HL1^-$ (Scheme 3). Interestingly, such a coordination induced hydrolysis reaction in the presence of metal ions is not a routinely observable pathway and is not observed as part of previously reported compounds with H₃L. The in situ formed ligand HL1⁻ (Scheme 1, right) originates from the hydrolysis of one

Compound	1	2	3 ·2MeOH
Formula	C ₂₄ H ₃₂ Ni ₂ N ₈ O ₈	C24H32Ni2N2O8Br2	C ₆₀ H ₉₀ Ni ₇ N ₈ O ₁₈ ·4(NO ₃)·2(MeOH)
т	677.99	753.75	1934.49
Space group	$P2_1/n$	$P2_1/c$	C2/c
Crystal system	monoclinic	monoclinic	monoclinic
a (Å)	8.807(2)	8.986(2)	26.1425(15)
b (Å)	15.001(3)	15.349(4)	21.0145(12)
<i>c</i> (Å)	11.577(3)	11.009(3)	16.1156(9)
α (°)	90.00	90.00	90.0
β(°)	109.301(5)	113.874(7)	104.2888(16)
γ (°)	90.00	90.00	90.0
U (Å ³)	1443.6(6)	1388.5(6)	8579.6(8)
T (K)	293	293	293
Ζ	2	2	4
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.560	1.803	1.498
F(000)	704	760	4024
Crystal size (mm)	$0.39 \times 0.26 \times 0.13$	$0.43 \times 0.36 \times 0.18$	$0.40 \times 0.32 \times 0.19$
μ (Mo K α) (cm ⁻¹)	13.65	42.83	15.87
Measured refl.ns	17380	20115	33 392
Unique ref.ns	4445	4220	5571
R _{int}	0.0365	0.0474	0.0413
Obs. refl.ns $I \ge 2\sigma(I)$]	2291	2667	4236
$\theta_{\min} - \theta_{\max}$ (°)	2.31-31.91	2.42-31.50	1.61-22.50
hkl Ranges	-12, 12; -22, 19; -17, 15	-12, 12; -21, 21; -15, 16	-28, 28; -22, 22; -17, 16
$R(F^2)$ (Obs.Refl.ns)	0.0601	0.0416	0.0976
$wR(F^2)$ (All refl.ns)	0.2469	0.1158	0.2930
No. variables	206	184	524
Goodness of fit	1.136	1.013	1.094
$\Delta ho_{ m max}$; $\Delta ho_{ m min}$ (e Å $^{-3}$)	0.784; -1.265	1.014; -0.576	0.829; -1.667
CCDC No.	902757	869970	902758

 $R_1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|. \ wR_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o)^2]^{1/2}. \ w = 0.75 / (\sigma^2(F_o) + 0.0010F_o^2).$



Scheme 3. Schematic representation of two different courses of reaction for $\{Ni_2\}$ and $\{Ni_7\}$ assemblies.

of the imine arms of H_3L , as assisted in all probability by the coordination of nickel(II) ions. Change of metal salt from Ni(NO₃)₂·6H₂O to NiBr₂·3H₂O could not stop the ligand arm hydrolysis.

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$$\begin{split} & 2H_{3}L + 2Ni(NO_{3})_{2} \cdot 6H_{2}O + 2NaN_{3} + 2NEt_{3} \\ & \rightarrow [Ni_{2}(N_{3})_{2}(\mu\text{-}HL1)_{2}(OH_{2})_{2}] + 2(HNEt_{3})(NO_{3}) \\ & + 2NH_{2}(CH_{2})_{3}OH + 2NaNO_{3} + 10H_{2}O \end{split}$$

$$\begin{array}{l} 2H_{3}L+2NiBr_{2}\cdot 3H_{2}O+2NEt_{3}\rightarrow [Ni_{2}Br_{2}(\mu\text{-}HL1)_{2}(OH_{2})_{2}]\\ \\ +2(HNEt_{3})(Br)\\ \\ +2NH_{2}(CH_{2})_{3}OH+4H_{2}O \end{array} \tag{2}$$

Formation of 1 and 2 as electro-neutral compounds was further confirmed from the elemental analysis and molar conductivity measurements and by the single crystal X-ray structure determinations (vide infra). When the reaction of Ni(NO₃)₂·6H₂O was carried out with H_3L in MeOH in presence of NEt₃ as base, **3** was obtained. Keeping in mind the formation of 1 and 2, several other H₃L/Ni(NO₃)₂·6H₂O/NEt₃ ratios were explored, and we report here the optimized one that gave a clean and characterizable product in high yield. At room temperature, complex **3** is isolated by stirring a methanolic solution of a mixture of the above stated components in a 4:7:4 molar ratios for 2.5 h. The complex precipitates directly from the reaction mixture as a green solid in \sim 68% yield. The synthesis of **3** from H_{3L} is summarized in Eq. (3), considering the non-hydrolytic behavior of the ligand as opposed to the process dominant in previous two cases and generation of hydroxido bridges from the water molecule present in the solvent during the complexation reaction.

$$\begin{array}{l} 4H_{3}L+7Ni(NO_{3})_{2}\cdot 6H_{2}O+4NEt_{3}+2MeOH\\ \rightarrow [Ni_{7}(\mu_{3}\text{-}OH)_{6}(\mu\text{-}H_{2}L)_{4}](NO_{3})_{4}\cdot 2MeOH+4(HNEt_{3})\\ \times (NO_{3})+6HNO_{3}+36H_{2}O \end{array} \tag{3}$$

The elemental analysis and molar conductivity data are consistent with the formula $[Ni_7(\mu_3-OH)_6(\mu-H_2L)_4](NO_3)_4$ ·2MeOH for **3**·2MeOH and the existence of tetra-cationic complex species was further confirmed from X-ray structure determination. The molar conductivity value (Λ_M) [32] for **3** in MeOH is 391.5 Ω^{-1} cm² mol⁻¹ which is slightly lower than the prescribed value for 1:4 electrolyte behavior. The nature of the final reaction product as **3** is greatly influenced by the stabilization of the H₂L⁻, solvent system used, generation of hydroxido groups and the sequence of addition of the reactants.

3.2. Description of the crystal structures

Single crystals suitable for X-ray structure determination were obtained by slow evaporation of saturated MeOH solutions of **1**, **2** and **3** after three and two weeks, and 18 days, respectively. The selected bond lengths and bond angles are collected in Table 2.

3.2.1. [Ni₂(N₃)₂(µ-HL1)₂(OH₂)₂] (1)

Complex 1 forms green crystals belonging to the monoclinic crystals system, space group $P2_1/n$. View of 1 with the atom-num-

Table 2 Selected inter-atomic di	istances (Å) and a	ngles (°) for complex 1 , 2	and 3 ·2MeOH.
1 Distances N(2)-Ni(1) O(3)-Ni(1) Ni(1)-O(1)	2.095(4) 2.037(3) 2.015(2)	Ni(1)-N(1) Ni(1)-O(1) ^a Ni(1)-O(2)	2.018(3) 2.024(3) 2.135(3)
$\begin{array}{l} Angles \\ O(1)-Ni(1)-O(1)^{a} \\ O(1)-Ni(1)-O(1)^{a} \\ O(1)-Ni(1)-O(3) \\ N(1)-Ni(1)-O(3) \\ N(1)-Ni(1)-O(3) \\ O(1)-Ni(1)-O(3) \\ O(1)-Ni(1)-N(2) \\ N(1)-Ni(1)-N(2) \\ N(1)-Ni(1)-N(2) \end{array}$	$\begin{array}{c} 90.20(12)\\ 81.14(12)\\ 170.75(12)\\ 169.98(12)\\ 99.62(13)\\ 88.94(12)\\ 88.53(16)\\ 93.75(18) \end{array}$	$\begin{array}{l} O(1)^{a}-Ni(1)-N(2)\\ O(3)-Ni(1)-N(2)\\ O(1)-Ni(1)-O(2)\\ N(1)-Ni(1)-O(2)\\ O(1)^{a}-Ni(1)-O(2)\\ O(3)-Ni(1)-O(2)\\ N(2)-Ni(1)-O(2)\\ \end{array}$	89.29(17) 92.79(18) 89.44(13) 92.42(16) 84.31(15) 88.16(14) 173.51(17)
2 Distances O(3)-Ni(1) O(2)-Ni(1) Ni(1)-N(1)	2.041(2) 2.117(3) 1.999(3)	Ni(1)-O(1) Ni(1)-Br(1) $O(1)^b-Ni(1)$	2.025(2) 2.6454(7) 2.014(2)
$\begin{array}{l} Angles \\ N(1)-Ni(1)-O(1)^b \\ N(1)-Ni(1)-O(1) \\ O(1)-Ni(1)-O(1)^b \\ N(1)-Ni(1)-O(3) \\ O(1)^b-Ni(1)-O(3) \\ O(1)-Ni(1)-O(3) \\ N(1)-Ni(1)-O(2) \\ O(1)^b-Ni(1)-O(2) \\ O(1)^b-Ni(1)-O(2) \end{array}$	$170.41(10) \\91.00(10) \\79.71(10) \\99.97(11) \\89.23(10) \\168.83(9) \\90.49(13) \\87.41(12)$	O(1)-Ni(1)-O(2) O(3)-Ni(1)-O(2) N(1)-Ni(1)-Br(1) O(1) ^b -Ni(1)-Br(1) O(1)-Ni(1)-Br(1) O(3)-Ni(1)-Br(1) O(2)-Ni(1)-Br(1)	91.70(11) 86.17(12) 90.66(9) 92.18(7) 92.78(7) 89.20(8) 175.35(9)
3-2MeOH Distances Ni(1)-O(8) Ni(1)-O(9) Ni(1)-O(9) ^c Ni(1)-O(9) ^c Ni(1)-O(7) ^c Ni(2)-N(2) Ni(2)-N(2) Ni(2)-O(8) Ni(2)-O(1) Ni(2)-O(7) Ni(2)-O(6) ^c Ni(2)-O(3)	2.047(7) 2.047(7) 2.062(6) 2.062(6) 2.076(7) 1.997(10) 2.015(7) 2.043(6) 2.066(6) 2.079(8) 2.095(7)	$\begin{array}{l} Ni(3)-N(1)\\ Ni(3)-O(8)\\ Ni(3)-O(4)^c\\ Ni(3)-N(4)^c\\ Ni(3)-O(1)\\ Ni(3)-O(1)\\ Ni(4)-O(4)\\ Ni(4)-O(4)\\ Ni(4)-O(9)\\ Ni(4)-N(3)\\ Ni(4)-O(7)\\ Ni(4)-O(5)\\ Ni(4)-O(2)^c\\ \end{array}$	2.044(9) 2.052(6) 2.059(7) 2.059(8) 2.066(7) 2.095(6) 2.005(6) 2.018(7) 2.018(9) 2.090(6) 2.092(7) 2.160(8)
		(contin	ued on next page)

Angles			
O(8)-Ni(1)-O(8) ^c	93.4(4)	N(1)-Ni(3)-O(8)	164.9(3)
O(8)-Ni(1)-O(9)	166.3(3)	$N(1)-Ni(3)-O(4)^{c}$	101.1(3)
$O(8) - Ni(1) - O(9)^{c}$	82.0(3)	$O(8)-Ni(3)-O(4)^{c}$	92.0(3)
$O(8)^{c} - Ni(1) - O(9)$	82.0(3)	$N(1)-Ni(3)-N(4)^{c}$	89.7(3)
$O(8)^{c} - Ni(1) - O(9)^{c}$	166.3(3)	$O(8)-Ni(3)-N(4)^{c}$	98.2(3)
$O(9)-Ni(1)-O(9)^{c}$	105.2(4)	$O(4)^{c} - Ni(3) - N(4)^{c}$	88.6(3)
$O(8)^{c}-Ni(1)-O(7)^{c}$	94.7(3)	N(1)-Ni(3)-O(1)	88.2(3)
$O(8)-Ni(1)-O(7)^{c}$	84.7(3)	O(8)-Ni(3)-O(1)	78.2(3)
O(9)-Ni(1)-O(7)	82.9(3)	$O(4)^{c}-Ni(3)-O(1)$	169.5(3)
$O(9)^{c}-Ni(1)-O(7)$	97.7(3)	$N(4)^{c}-Ni(3)-O(1)$	96.5(3)
$O(8)^{c}-Ni(1)-O(7)^{c}$	84.7(3)	$N(1)-Ni(3)-O(9)^{c}$	93.8(3)
$O(8)-Ni(1)-O(7)^{c}$	84.7(3)	O(8)-Ni(3)-O(9) ^c	81.1(3)
$O(9)-Ni(1)-O(7)^{c}$	97.7(3)	$O(4)^{c} - Ni(3) - O(9)^{c}$	79.2(3)
$O(9)^{c}-Ni(1)-O(7)^{c}$	82.9(3)	$N(4)^{c}-Ni(3)-O(9)^{c}$	167.8(3)
O(7)-Ni(1)-O(7)	179.0(4)	O(1)-Ni(3)-O(9) ^c	95.3(3)
N(2)-Ni(2)-O(8)	171.1(3)	O(4)-Ni(4)-O(9)	82.3(3)
N(2)-Ni(2)-O(1)	91.5(3)	O(4)-Ni(4)-N(3)	92.3(3)
O(8)-Ni(2)-O(1)	79.6(3)	O(9)-Ni(4)-N(3)	174.4(4)
N(2)-Ni(2)-O(7)	92.4(3)	O(4)-Ni(4)-O(7)	96.1(3)
O(8)-Ni(2)-O(7)	85.7(3)	O(9)-Ni(4)-O(7)	83.6(3)
O(1)-Ni(2)-O(7)	87.5(3)	N(3)-Ni(4)-O(7)	97.5(3)
$N(2)-Ni(2)-O(6)^{c}$	87.4(4)	O(4)-Ni(4)-O(5)	175.5(3)
$O(8)-Ni(2)-O(6)^{c}$	94.6(3)	O(9)-Ni(4)-O(5)	93.5(3)
$O(1)-Ni(2)-O(6)^{c}$	93.5(3)	N(3)-Ni(4)-O(5)	91.9(3)
$O(7)-Ni(2)-O(6)^{c}$	179.0(3)	O(7)-Ni(4)-O(5)	85.0(3)
N(2)-Ni(2)-O(3)	95.4(3)	O(4)-Ni(40-O(2) ^c	89.6(3)
O(8)-Ni(2)-O(3)	93.4(3)	O(9)-Ni(4)-O(2) ^c	94.3(3)
O(1)-Ni(2)-O(3)	173.1(3)	N(3)-Ni(4)-O(2) ^c	85.2(3)
O(7)-Ni(2)-O(3)	92.1(3)	O(7)-Ni(4)-O(2) ^c	173.6(3)
$O(6)^{c}-Ni(2)-O(3)$	86.9(3)	$O(5)-Ni(4)-O(2)^{c}$	89.0(3)

$$a^{a} 1 - x, -y, 2 - z$$

^b 1 - x, -y, 1 - z. ^c 1 - x, y, 1.5 - z.

 $1 - x, y, 1 \cdot 3 - 2.$

bering scheme is given in Fig. 1. The structure consists of a hydrolyzed ligand bridged $[Ni_2(N_3)_2(\mu-HL1)_2(OH_2)_2]$ complex as a neutral aggregate with the Ni^{II} cations linked together by the action of two O₂N donor binucleating ligands HL1⁻ (Fig. S1). The asymmetric unit consists of one-half of the dinuclear unit and the second half of the dimer is generated by symmetry operations (1 - x, -y, 2 - z).

The two bridging functions are accomplished by the central phenoxido moiety of HL1⁻, while the imine N and carbonyl O atoms at opposite sides contribute two other coordination sites. Exogenous azido N and water O atoms fulfil the hexacoordination around each Ni ion. Each Ni atom is in a N₂O₄ environment with the two octahedrons sharing the edge defined by the bridging phenolate oxygen atoms (Fig. 1). The equatorial planes intersecting at this edge form an angle of 180°. The geometric restrictions resulting from the symmetrical dispositions of two HL1⁻ provide a Ni-O-Ni angle of 98.8° but the O-Ni-O angle is shorter at 81.12°. The Ni-O (carbonyl) separations at 2.03 Å are similar to other reported values [33]. The water molecules are loosely bound at 2.13 Å (Fig. S1). The azido ligands, opposite to water ligands, at 2.095 Å indicate a tetragonally elongated octahedron around nickel(II) ions (Figs. S1 and S2). The intramolecular Ni···Ni distance is 3.068 Å. Intermolecular hydrogen bonds are absent within the crystal lattice due to the absence of any lattice solvent molecules (Fig. S3).

3.2.2. $[Ni_2Br_2(\mu-HL1)_2(OH_2)_2]$ (2)

Complex **2** forms green crystals in monoclinic $P2_{1/c}$ crystal system. It is a dinuclear aggregate of Ni^{II} ions bridged and chelated by the hydrolyzed ligands HL1⁻ in a manner as in complex **1**. The face-to-face orientations of two hydrolyzed ligands bind two Ni(II) ions leaving behind two other coordination sites for anion and water coordination. Two such octahedral units share the phenoxido bridged O···O edge (Fig. S4). View of **2** with the atom-numbering



Fig. 1. View of $[Ni_2(N_3)_2(\mu-HL1)_2(OH_2)_2]$ unit in **1** with partial atom-numbering scheme. H atoms are omitted for clarity. Color code: Ni green, N blue, O red, C black. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. Structure of $[Ni_2(Br)_2(\mu-HL1)_2(OH_2)_2]$ unit in **2** with partial atom-numbering scheme. H atoms are omitted for clarity. Color code: Ni green, N blue, O red, Br dark yellow, C black. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

scheme is given in Fig. 2. The asymmetric unit consists of one-half of the dinuclear unit and no interstitial solvent molecule. The second half of the dimer is generated by symmetry operations (1 - x, -y, 1 - z).

The groups below and above the ligand planes register longer distances (Ni–O_{water}, 2.12 Å; Ni–Br, 2.64 Å) compared to those from $HL1^-$ (Ni–O_{carbonyl}, 2.04 Å; Ni–O_{phenoxido}, 2.01 and 2.02 Å; Ni–N_{imine}, 1.99 Å) (Fig. S4). The dihedral angles between intersecting equatorial planes is 180°; the bridging Ni–O–Ni angle is 100.2°, and the Ni…Ni separation is 3.101 Å. The trigonal planar orientation of the bridging phenoxido oxygen atoms keep the phenyl rings coplanar with the *basal* O₃N planes around each nickel(II) ion. No special hydrogen bonding network was observed within the crystal lattice of **2** (Fig. S5).

3.2.3. $[Ni_7(\mu_3-OH)_6(\mu-H_2L)_4](NO_3)_4 \cdot 2MeOH (3 \cdot 2MeOH)$

The green plate-like crystals of **3** crystallize in the monoclinic space group *C2/c*. The molecular structure of the compound **3**·2MeOH is shown in Fig. 3. The structure consists of a heptametallic tetra-cationic $[Ni_7(\mu_3-OH)_6(\mu-H_2bpmp)_4]^{4+}$ part and four NO₃⁻ anions. The asymmetric unit consists of one-half of the heptanuclear unit and two MeOH solvent molecules. The second half of the heptamer is generated by symmetry operations (1 - x, y, 1.5 - z).



Fig. 3. Molecular structure of $[Ni_7(\mu_3-OH)_6(\mu-H_2L)_4]^{4+}$ unit viewed perpendicular (top) and parallel (bottom) to the best $[Ni_7]$ plane in **3**·2MeOH with partial atomnumbering scheme. H atoms are omitted for clarity. Color code: Ni green, N blue, O red, C gray. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The core in **3** is best described as a body centered hexagon where by six Ni^{II} ions surround a central Ni^{II} centre to form an arrangement featuring four fused defective cubanes (Fig. S6). Topologically analogous [Ni₇] complexes are known with different organic shell ligands [17,34a-c]. In a strained cluster-like arrangement all Ni^{II} centers enjoy octahedral geometries. The six μ_3 -bridging OH⁻ ions (05, 08 and 09 and symmetry equivalents, s.e.) link the central nickel (Ni1) to the six peripheral nickel ions (Ni2, Ni3 and Ni4 and s.e.). The central Ni^{II} ion is located at a site with imposed C₂ symmetry. Out of the six bridging HO⁻ ions around the central Ni^{II} ion functioning as a trap in the cluster growth, four are squeezed trigonal pyramidal (solid angle around O atom are 294.16° and 297.6°) and two are planar T-shaped (solid angle around O atom is 352.4°) connectors (Fig. 3). The four singly deprotonated (at the phenolate site) H_2L^- ligands bridge the peripheral Ni^{II} centres. Thus six hydroxido and four phenoxido oxygen atoms complete the $[Ni_7O_{10}]$ core (Fig. S7), where the bridging is ensured by six (O_6) bridging hydroxido (μ_3 -mode) and four (O4) phenoxido bridges. The remaining coordination sites of the octahedral Ni^{II} ions are completed by peripheral imine groups and alcohol residues (from H_2L^-) making the ligand μ_3 -bridging. Within the [Ni₇O₁₀] nickel-oxygen core the Ni…Ni distances range from 3.00 to 3.15 Å and the Ni-O-Ni angles span the range of 93.10-102.07° (Fig. 4).



Fig. 4. The Ni₇ skeleton of 3 2MeOH showing all the inter-metallic distances.

Interestingly, all the protonated alcohol arms of the ligand $H_2L^$ remain coordinated to the Ni^{II} ions and show hydrogen-bonding interactions with the methanol oxygen (O1A) atom is bonded to (H)O6 at a O···O separation of 2.694 Å. The pendent ligand alcohol arms (H)O2, (H)O3 and (H)O5 are hydrogen bonded to O11(NO₃), O15(NO₃) and O13(NO₃) at the O···O separation of 2.612, 2.625 and 2.712 Å, respectively. The complex crystallizes with two solvent methanol molecules which are hydrogen bonded to the oxygen atoms of the ligand alcohol arm. One of the methanol oxygen (O1A) atom is suitably hydrogen bonded to ligand (H)O6 at a O···O separation of 2.694 Å. The same methanol oxygen (O1A) atom shows hydrogen bonding interactions with lattice water oxygen (O1B) at 2.749 Å. Near the [Ni₇] unit the lattice water and methanol molecules establish hydrogen-bonding network through interactions with NO₃⁻ groups (Fig. S8).

These hydrogen-bonding interactions provide an aesthetically pleasing 3D network structure (Figs. S8 and S9). A space-filling diagram of 3.2MeOH along the crystallographic b-axis identifies the compactness of the seven metal atoms (Fig. S10). Inspection of Fig. 3 suggests indeed that the formation of 3 occurs through trapping of two such trinuclear fragments $[Ni_3(OH)_2(\mu-H_2L)_2]^{2+}$, very much similar to our recently reported [Zn₃] complex [35a-c, 36], by in situ generated Ni(OH)₂ template (Scheme S2). While the four μ_3 -trigonal pyramidal HO⁻ bridging modes present in this complex are quite common, the planar T-shaped feature observed in 3 (Fig. S11) is rather exceptional. The unique hexagonal Ni7 arrangement (Fig. S6) of complex 3 results from the peculiar preferences of H_2L^- in front of the Ni^{II}/HO⁻ system, as opposed to other wellestablished structures observed for Ni^{II} clusters with similar sets of ligands, such as discs [17,35a] and others [36]. The O-Ni-O angles on the other hand are different within 81.9-175.1° and not observed in other structures. The Ni–O bond lengths involving μ_3 -OH linkers remain within 2.00–2.09 Å. The metallic skeleton and two views of the core of complex 3 2MeOH are illustrated in Figs. S7 and S12, respectively.

3.3. FT-IR spectroscopy

The broad and sharp peaks in the FT-IR spectra of **1** and **2** at 3401, 3424 and 1642 and 1639 cm⁻¹ are due to the stretching modes characteristic of the uncoordinated ligand O–H and bound C=N functionalities of HL1⁻. In addition, complex **1** shows a very strong and sharp band at 2099 cm⁻¹ for the $\bar{\nu}as_{(N-N-N)}$ stretching vibration of the nickel(II) bound terminal N₃⁻ groups, while the symmetric vibration $\bar{\nu}s_{(N-N-N)}$ appears as a weak band at 1346 cm⁻¹ [37]. For complex **3** the sharp peak at 1638 cm⁻¹ is due to the $\nu_{C=N}$ stretching frequency of H₂L⁻ and a broad medium band centered at 3398 cm⁻¹ attributable to the ν_{OH} vibrations from the nickel(II) bound μ_3 -HO⁻ bridges, ligand OH groups and crystal lattice trapped water molecules. The very strong band at

 1383 cm^{-1} in **3** is indicative of the presence of ionic nitrates outside the coordination sphere [38].

3.4. Electronic UV-Vis spectra

Moderate solubility in MeOH of all the three complexes allowed us to record multiple optical absorption bands in the 200–900 nm regions. Broad absorption bands (λ), with maxima at 674 nm ($\varepsilon = 401 \text{ L} \text{mol}^{-1} \text{ cm}^{-1}$), 663 nm ($\varepsilon = 119 \text{ L} \text{mol}^{-1} \text{ cm}^{-1}$) and 673 nm ($\varepsilon = 417 \text{ L} \text{mol}^{-1} \text{ cm}^{-1}$) for **1**, **2** and **3**, respectively can be assigned to the spin-allowed ${}^{3}\text{A}_{2g}(\text{F}) \rightarrow {}^{3}\text{T}_{1g}(\text{F})$ transition consistent with their slightly distorted octahedral configurations. The ${}^{3}\text{A}_{2g}$ (F) $\rightarrow {}^{3}\text{T}_{2g}(\text{F})$ transitions usually appear above 700 nm region are systematically missing for all the three complexes [39]. The ${}^{3}\text{A}_{2g}$ (F) $\rightarrow {}^{3}\text{T}_{1g}(\text{P})$ transitions appear at 368 nm ($\varepsilon = 8519 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$), 372 nm ($\varepsilon = 1199 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$) and 371 nm ($\varepsilon = 1813 \text{ L} \text{ mol}^{-1}$ cm⁻¹) for **1**, **2** and **3**, respectively [33]. The intense absorptions at 260 nm ($\varepsilon = 67095 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$), are due to $\pi \rightarrow \pi^*$ transitions centered on the ligand back bone.

3.5. Spin density distribution analysis for possible magnetic interactions in **1** and **2**

In order to provide the magnetic coupling interactions theoretically, the spin density distribution is analyzed in compounds 1 and **2**. According to the molecular orbital theory, spin delocalization is the result of electron transfer from the magnetic centers to the ligand atoms. The spin densities of compounds 1 and 2 in the broken-symmetry state are summarized in Table 3, where positive and negative signs denote α and β spin states, respectively. It should be mentioned that for both complexes the antiferromagnetic singlet (two α electrons on one Ni and two β electrons on the other Ni) is energetically more stable than the high spin configuration (multiplicity 5). This difference is higher in compound 2 (-0.51 mHa) than in 1 (-0.34 mHa), therefore it is expected a larger (in absolute value) coupling constant / for compound 2. In Table 3 it is shown that the spin densities on the two Ni(II) ions in compounds 1 and 2 have similar absolute values but opposite signs. For instance in 1, the Ni1 atom is mainly populated by the unpaired electrons with α spin (1.688) and Ni1^{*} with β spin (-1.688). It is obvious that the unpaired electrons are mainly localized on each Ni(II) ions, which indicates that the Ni(II) ions are indeed the magnetic centers. The spin densities on the ligand (O1, O2W, O3, N1 and N2/Br1) atoms have the same signs as that of the Ni(II) atoms to which they are bonded, which reveals that there is spin delocalization from the Ni(II) ions to the ligands. In addition,

Table 3

The spin densities on the selected atoms for compounds 1 and 2 at the UB3LYP/6-31+G* level of theory.

Compound 1		Compound 2	
Atoms	Spin density	Atoms	Spin density
Ni1	1.688	Ni1	1.620
Ni1 [*]	-1.688	Ni1*	-1.620
01	0.038	01	0.044
01*	-0.038	01*	-0.044
02W	0.025	02W	0.028
02W*	-0.025	02W*	-0.028
N1	0.080	N1	0.097
N1 [*]	-0.080	N1*	-0.097
N2	0.037	Br1	0.115
N2*	-0.037	Br1*	-0.115
03	-0.007	03	-0.004
03*	0.007	03*	0.004

Symmetry equivalents.



Fig. 5. Spin density map computed for compounds 1 and 2 at the UB3LYP/6-31+ G^* level of theory.

the spin delocalization is strong enough that >18% of the spin for the unpaired electrons on the Ni(II) centers are delocalized to the ligand atoms. The spin densities on the Ni(II) centers in compound 1 (±1.688) are higher in absolute value than those of compound **2** (±1.620), which indicates that the differences between the antiferromagnetic singlet and the high spin state can be rationalized in terms of the spin density on the metal centers.

According to the active-electron approximation, it can be considered that in the bridged magnetic coupling systems, only the overlaps between the singly occupied molecular orbitals (SOMO) of the metal centers and the p orbitals of the ligands contribute to the magnetic coupling interaction. In octahedral Ni^{II}, the magnetic orbitals are formed by the $d_{x^2-v^2}$ and d_{z^2} orbitals, each containing an unpaired electron. Therefore, for the diphenoxidobridged compounds **1** and **2**, only the $d_{x^2-v^2}$ orbitals of the metal atoms and the local orbitals of the bridging ligand are involved in the magnetic coupling pathway. A theoretical confirmation of this explanation comes from the spin density map computed for compounds 1 and 2 (Fig. 5), that clearly agrees with the aforementioned mechanism. Unfortunately, for compound **3** the theoretical analysis of the spin density has been computationally unaffordable at this level of theory due to convergence problems in the calculations likely due to the large number of unpaired electrons (14) in the high spin state.

4. Concluding remarks

As part of the generation of self-assembled super structures based on ligated metal ion motifs, we have previously shown that reaction of H₃L with Zn^{II} leads to a novel Zn₃ complex. Now we have shown that the reaction with Ni^{II} is responsible for trapping of two such hitherto unknown trinuclear fragments $[Ni_3(OH)_2(\mu-H_2L)_2]^{2+}$ by in situ generated Ni(OH)₂ species for the generation of $[Ni_7(\mu_3-OH)_6(\mu_3-H_2L)_4](NO_3)_4$ ·2MeOH. Similar reactions in presence of externally added N₃⁻ and metal salt derived Br⁻ anions inhibit the growth of the heptametallic species and provided only basic dinuclear compounds $[Ni_2(N_3)_2(\mu-HL1)_2(OH_2)_2]$ and $[Ni_2Br_2$ $(\mu-HL1)_2(OH_2)_2]$ through hydrolysis of single imine arm of the ligand. These results clearly indicate the superiority of reaction medium derived hydroxido groups, as against azido and bromido groups, for cluster growth and hydrolysis of single ligand arm.

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Appendix A. Supplementary data

CCDC 902757, 869970 and 902758 contain the supplementary crystallographic data for **1**, **2** and **3**·2MeOH. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http:// dx.doi.org/10.1016/j.poly.2013.01.009.

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