Metal directed self-assembly of Tetranuclear Cu^{II} and Ni^{II} clusters

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Abstract. The self-assembly of two pyridine hydrazone based tritopic ligands appended with terminal carboxylate groups with Cu^{II} and Ni^{II} have been investigated. These polytopic ligands with tridentate coordination pockets were designed to produce homoleptic [3 × 3] grid complexes on reaction with transition metals. Despite the formation of anticipated metallogrids as the final self-assembly outcome, metal ion geometric preferences and ligand flexibility lead to the formation of tetranuclear clusters in the self-assembly process with Cu^{II} and Ni^{II} metal ions. These results illustrate the dynamic nature of the metal–ligand interactions and flexible nature of the ligand backbone in coordination self-assembly. The synthesis, structure and magnetic properties of three tetraanuclear species {[Cu₄(H₂L^{1b})₂(OTf)₄(OH)₂(H₂O)₂·6H₂O]_n (**1**), [Ni₄(L^{2a})₂(OCH₃)₄·4H₂O (**2**), [Cu₄(L^{2b})₂(OTf)₄(H₂O)₄·6H₂O (**3**) involving two tritopic ligands with central pyridine framework are described.

Keywords. Polytopic hydrazone-based ligands; self-assembly; tetranuclear clusters; X-ray structure; magnetic properties.

1. Introduction

Grid-type metal ion architectures in which a set of metal ions are held together in a regular framework by the perpendicular arrangement of polytopic organic ligands have been proposed as promising candidates, because of their potentially useful electronic, magnetic and photophysical properties.^{1,2}

In this context, our interest has been targeted to develop new synthetic methodologies to high nuclearity [n × n] metallogrids, particularly methods that might also allow some level of control over the metal oxidation state and its electronic spin state. Apart from the inherent synthetic challenge, our main interest is to achieve a range of high nuclearity metallogrids with high ground spin state and the study of progressive changes in their magnetic and electronic properties. This requires expansion of the nuclearity of the metallogrid, and effectively rules out using close capped terminal functionalities in the ligand framework, which is much less feasible for larger grids since it requires a correspondingly larger ligands which are associated with synthetic challenges. Instead,

we have been exploring the substitution of ester/oxime functions at the terminal position of the ligand framework. Since ester/oxime groups possess the multiple binding capabilities and would likely affect the nuclearity of the grid and yield an extended architecture.³ A previous use of diacetyl monoxime and methyl pyruvate terminal functions of picolinic/pyrimidine hydrazone ligands in Ni, Mn and Co chemistry had provided the extended grid architectures 3 × [2 × 2] Ni₁₂,³ and [3 × 3]_n {Mn₁₂}_n⁴ generated through intergrid linkage of the grid subunits. On the other hand, polydentate ligands with flexible linker groups positioned between terminal donor units can coordinate in a variety of binding modes and they self-assemble to generate helicates,^{5,6} clusters^{7–9} and grids,^{10,11} based on the positioning of the terminal donor sets. Polytopic picolinic hydrazone based ligands with adjacent coordination pockets separated by single atom bridging group like alkoxides allow the alignment of metal centres in linear fashion with the formation of stable five-membered chelate rings. They self-assemble to generate regular square tetranuclear [2 × 2] and nonanuclear [3 × 3] grids

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Scheme 1. Structures of ligands and their hydrolyzed counterparts.

based on the number of coordination pockets available for binding.^{12–19} Alkoxide bridges bring the metal ions into close proximity leading to intramolecular magnetic exchange interactions. However, in some cases, competitive metal–ligand reactions can lead to a different self-assembly outcome.^{20–22}

The present work deals with the synthesis and study of two tritopic ligands designed based on pyridine framework (Scheme 1). Notable examples of some nongrid tetra Cu^{II} and Ni^{II} complexes are discussed in detail.

2. Experimental

2.1 Materials

All the chemicals were obtained from commercial sources and used as received. Solvents were purified using standard literature methods.

2.1a Synthesis of ligand H_2L^1 and H_2L^2 : Both the ligands H_2L^1 and H_2L^2 were prepared by following our previously reported procedure without any further modification.⁴

2.1b Synthesis of $[\text{Cu}_4(\text{H}_2\text{L}^{1b})_2(\text{OTf})_4(\text{OH})_2(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ (1): Ligand H_2L^1 (100 mg, 0.254 mmol) was added to the clear solution of $\text{Cu}(\text{OTf})_2$ (275 mg, 0.763 mmol) in 10 mL MeNO_2 forming a clear light blue colored solution and the reaction mixture was stirred for 30 min at 50 °C. The light blue solution thus formed was filtered and left in open air for slow evaporation. Blue-green crystals suitable for X-ray structural analysis were formed after 24 h. (Yield: 76%)

Anal. Calcd. for $\text{C}_{26}\text{H}_{36}\text{Cu}_4\text{F}_{12}\text{N}_{10}\text{O}_{32}\text{S}_4$: C, 19.38; H, 2.25; N, 8.69%. Found. C, 19.12; H, 2.65; N, 8.50%. IR (ν , cm^{-1}): 3501.15 (H_2O); 1674.56 ($\text{C}=\text{O}$); 1644.45 ($\text{C}=\text{N}$).

2.1c Synthesis of $[\text{Ni}_4(\text{L}^{2a})_2(\text{OCH}_3)_4] \cdot 4\text{H}_2\text{O}$ (2): Ligand H_2L^2 (50 mg, 0.137 mmol) was added to the solution of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (68 mg, 0.275 mmol) in 8 mL of MeOH/MeCN (1:1) mixture forming a clear deep red colored solution. The reaction mixture was stirred for 30 min at 50 °C. A deep-red solution formed, which was filtered and kept for crystallization by slow evaporation. A dark red microcrystalline solid formed after three days (Yield: 73%). X-ray quality crystals for structural analysis were obtained by slow diffusion of diethyl ether into the methanolic solution of the complex. Calcd. for $\text{C}_{30}\text{H}_{30}\text{N}_{10}\text{Ni}_4\text{O}_{18}$: C, 34.21; H, 2.87; N, 13.30%. Found. C, 33.89; H, 3.22; N, 2.53%. IR (ν , cm^{-1}): 3418.83 (H_2O); 1625.67 ($\text{C}=\text{O}$); 1603.57 ($\text{C}=\text{N}$).

2.1d Synthesis of $[\text{Cu}_4(\text{L}^{2b})_2(\text{OTf})_4(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ (3): Ligand H_2L^2 (100 mg, 0.275 mmol) was added to the solution of $\text{Cu}(\text{OTf})_2$ (298 mg, 0.826 mmol) in 10 mL MeNO_2 forming a clear light blue coloured solution. The reaction mixture was stirred for 30 min at 50 °C. The solution was filtered and left in open air for slow evaporation. X-ray quality light blue crystals were collected after 24 h. (Yield: 64%). Anal. Calcd. for $\text{C}_{24}\text{H}_{36}\text{Cu}_4\text{F}_{12}\text{N}_{10}\text{O}_{30}\text{S}_4$: C, 18.54; H, 2.33; N, 9.01%. Found. C, 18.14; H, 2.82; N, 8.74%. IR (ν , cm^{-1}): 3424.20 (H_2O); 1681.07 ($\text{C}=\text{O}$); 1638.57 ($\text{C}=\text{N}$).

2.2 Instrumentation

Standard schlenk line techniques were used to carry out the reactions in inert conditions. Melting points were measured

using BUCHI M-500. Fourier transform infrared (FT-IR) spectra were recorded on a BRUKER ALPHA-T FT-IR spectrometer with KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 NMR spectrometer. Elemental analysis was performed using Elementar vario MICRO cube CHN analyzer. Electrospray ionization mass spectrometry (ESI-MS) spectra of the compounds were recorded on a Bruker microTOF-Q II mass spectrometer. Single crystal diffraction data were collected on a Bruker APEX SMART D8 Venture CCD diffractometer at a temperature of 110 K with graphite monochromated Mo $K\alpha$ radiation. Variable-temperature (2–300 K) magnetic measurements were carried out for complex **1** and complex **3** with a Quantum Design PPMS magnetometer in DC mode using a field strength 0.5 T with appropriate corrections for the sample holder and diamagnetic contributions.

2.3 X-ray structure solution and refinement

Diffraction intensities of complex **1**, **2** and **3** were collected at 110.0(2) K on a Bruker Kappa APEX II Charge-Coupled Device (CCD) area-detector diffractometer controlled by the APEX2 software package²³ using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and equipped with an Oxford Cryosystems Series 700 cryostream. Diffraction images were processed with the software SAINT+²³ and absorption correction was performed using the empirical method implemented in SADABS.²⁴ The structures were solved by direct methods and refined by full-matrix least squares methods on F^2 using SHELXTL²⁵ package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions and refined on a riding model with isotropic thermal parameters twenty percent larger than the U_{eq} of the attached non-hydrogen atom. Crystal data and cell parameters for complexes **1**–**3** are listed in Table 1.

3. Results and Discussion

Tritopic ligands H_2L^1 and H_2L^2 involving the dipicolinic hydrazone framework appended with terminal pyruvate groups have coordination pockets suitably liable to attract three metal ions in a linear arrangement with two readily ionizable protons, therefore allowing it to act as a di-anionic ligand. Ligands H_2L^1 and H_2L^2 have the potential to bind metal ions in different modes with the involvement of the ligand's terminal open chain functions and the possibility of simultaneous coordination of the terminal esters to two metals to facilitate the inter-grid linkages resulting in an extended network-like structure. In the case of Mn(II), both the ligands self-assembled into an anticipated $[3 \times 3]$ metallogrid architectures. Both the ligands, H_2L^1 and H_2L^2 got hydrolyzed during the course of metallation and

self-assembled into polymeric and discrete metallogrid compounds based on the $[3 \times 3]$ Mn(II) square grid motif and with additional manganese(II) ions linked to the grid core (Scheme 2).⁴

But in the case of Copper and Nickel, the ligands resulted in tetranuclear complexes in an unexpected self-assembly process involving two ligands and four metal ions forming a diamond-like structure (Scheme 2). The dramatic difference between the self-assembly outcome in the manganese (square $[3 \times 3]$ metallogrids) and copper and nickel cases (tetranuclear cluster) is worth mentioning.

Apart from the coordination information encoded in the ligand framework, metal ion coordination algorithm also plays a crucial role in the self-assembly outcome. The present results emphasize the role of coordination geometry preferences of the metal ion and flexibility of the ligand backbone on the self-assembly product.

The diverse coordination abilities of manganese, nickel and copper to take advantage of the pool of donor atoms available when reacted with the large multidentate ligands results in a variety of self-assembly outcome. This, in turn, relates the balance between the hardness/softness of the metal ion and crystal field effects during the complex formation. Because of its coordination geometry flexibility, copper forms four, five and six coordinated geometries to allow the distortions; whereas, nickel is constrained by its limited coordination flexibility. From HSAB principle, Ni(II), soft centre prefers to coordinate with N, (soft base) as compared to O (hard base) and also attains the greater CFSE ($\Delta = -12 \text{ Dq}$). In the present study, H_2L^2 presents both nitrogen and oxygen donor atoms, but Ni(II) prefers to maximize its nitrogen donor content by leaving the hydrazone oxygen atoms uncoordinated. In contrast, manganese has nothing to gain in CFSE ($\Delta = 0 \text{ Dq}$) upon coordination, which is witnessed by the formation of $[3 \times 3]$ metallogrid architectures with both the tritopic ligands H_2L^1 and H_2L^2 . Coordination flexibility of the ligand backbone and metal-ion geometric preferences hindered the grid formation resulting in thermodynamically favoured cluster complexes.

The increased flexibility of the ligand might act to hinder the grid assembly. Higher order grids have not yet been witnessed with terminal open chain ligands and may require different reaction conditions (solvent, pH, temperature, etc.).

3.1 Description of Crystal Structure of $\{[\text{Cu}_4(\text{H}_2\text{L}^{1b})_2(\text{OTf})_4(\text{OH})_2(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}\}_n$ (**1**)

The structural representation of complex **1** is shown in Figure 1, and important metrical parameters are

Table 1. Crystallographic details for complexes 1–3.

Parameters	$\{[\text{Cu}_4(\text{H}_2\text{L}^{\text{lb}})_2(\text{OTf})_4(\text{OH})_2(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}\}_n(1)$	$[\text{Ni}_4(\text{L}^{2a})_2(\text{OCH}_3)_4] \cdot 4\text{H}_2\text{O} (2)$	$[\text{Cu}_4(\text{L}^{2b})_2(\text{OTf})_4(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O} (3)$
Empirical formula	$\text{C}_{26}\text{H}_{20}\text{Cu}_4\text{F}_{12}\text{N}_{10}\text{O}_{32}\text{S}_4$	$\text{C}_{30}\text{H}_{30}\text{Ni}_4\text{N}_{10}\text{O}_{18}$	$\text{C}_{24}\text{H}_{36}\text{Cu}_4\text{F}_{12}\text{N}_{10}\text{O}_{30}\text{S}_4$
Formula weight	1594.92	1053.48	1555.02
Temperature (K)	110(0)	110(0)	110(0)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space gr.	Triclinic, P-1	Monoclinic, P2 ₁ /c	Triclinic, P-1
Unit cell dimensions	a = 8.6987(12) Å, b = 9.9372(12) Å, c = 15.926(2) Å, α = 79.998(4)° β = 80.146(4)° γ = 86.165(4)°	a = 8.5077(16) Å, b = 25.570(5) Å, c = 18.744(4) Å, α = 90.0° β = 99.586(5)° γ = 90.0°	a = 8.7571(5) Å, b = 9.8355(5) Å, c = 15.9607(8) Å, α = 81.952(2)° β = 80.671(2)° γ = 86.712(2)°
Volume (Å ³)	1334.8(3)	4020.7(14)	1342.31(12)
Z, Calculated density (g/cm ³)	2, 1.984	4, 1.740	2, 1.924
Absorption coefficient (mm ⁻¹)	1.874	1.932	1.858
F(000)	1580	2144	1556
Crystal size (mm ³)	0.2 x 0.2 x 0.2	0.4 x 0.3 x 0.3	0.3 x 0.2 x 0.2
Theta range for data collection	2.27 to 28.34°	1.94 to 30.86°	2.31 to 26.77°
Limiting indices	−11 ≤ h ≤ 11, −13 ≤ k ≤ 13, −21 ≤ l ≤ 21	−12 ≤ h ≤ 12, −36 ≤ k ≤ 36, −26 ≤ l ≤ 26	−10 ≤ h ≤ 10, −12 ≤ k ≤ 12, −20 ≤ l ≤ 19
Reflections collected / unique	45498/6642	160478 / 12417	38857 / 5395
Completeness to theta	[R(int) = 0.0567]	[R(int) = 0.0611]	[R(int) = 0.0548]
Absorption correction	99.7%	98.1%	94.2%
Refinement method	Empirical	Empirical	Empirical
Data / parameters	Full-matrix least-squares on F ² 6642/399	Full-matrix least-squares on F ² 12417/567	Full-matrix least-squares on F ² 5395/380
Goodness-of-fit on F ²	1.028	1.080	1.024
Final R indices [I > 2 σ (I)]	R1 = 0.0829, wR2 = 0.2026	R1 = 0.0482, wR2 = 0.1192	R1 = 0.0510, wR2 = 0.1185
R indices (all data)	R1 = 0.1055, wR2 = 0.2192	R1 = 0.0578, wR2 = 0.1240	R1 = 0.0945, wR2 = 0.1369
Largest diff. peak and hole (e.Å ⁻³)	3.506 and −2.696	3.113 and −1.567	0.606 and −0.559

$$RI = \sum [|F_o| - |F_c|] / \sum [|F_o|], \quad wR2 = \left[\sum \left[w(|F_o|^2 - |F_c|^2)^2 \right] / \sum \left[w(|F_o|^2)^2 \right] \right]^{1/2}.$$

Scheme 2. Schematic representation of self-assembly of ligand H_2L^2 with $Mn(II)$,⁴ $Ni(II)$ and $Cu(II)$ metal ions.

Figure 1. Structural representation of complex **1** (left), core structure (middle) and Polymeric expansion view (right).

listed in Table 1. The single-crystal X-ray diffraction study shows that the structure consists of a 1D chain resulting from the bridging of the tetranuclear repeating units $\{[Cu_4(H_2L^{1b})_2(OTf)_4(OH)_2(H_2O)_2] \cdot 6H_2O\}$. Polymeric structural representation is shown in (Figure 1). Tetranuclear core structure consists of four $Cu(II)$ ions in distorted octahedral geometry. Each terminal $Cu(II)$ ion is bound to a hydrolyzed ligand fragment (Figure 1), where hydrolysis has occurred at one of the hydrazone imine carbon site representing a mononuclear complex. Each ligand is acting in a twisted heptadentate manner and bridging the terminal metal centers with tridentate and bidentate ends through copper centers. The two mononuclear ($Cu2$) end fragments are connected through central, octahedral, six-coordinate copper ions ($Cu1$), positioned at an inversion centre resulting in a tetranuclear core. The terminal octahedral $Cu(II)$ ion coordinates to a tetradentate (N_3O) ligand pocket, comprising of pyridine, diazene nitrogen atoms and carboxylate oxygen atom in a basal plane with five and six-membered chelate rings.

3.2 Description of Crystal Structure of $[Ni_4(L^{2a})_2(OCH_3)_4] \cdot 4H_2O$ (**2**)

The structural representation of complex **2** is shown in Figure 2, and important metrical parameters are listed in Table 1. Despite the different ligand terminal functionality and different reaction conditions, the resulting complex structure is similar to that of tetranuclear cluster published by Zhao *et al.*²⁶ The diamond shaped core structure consists of four $Ni(II)$ centers held together by two octadentate (N_5O_3) ligand strands. Both the terminal pyruvate ester groups of the ligand got hydrolysed during the metalation resulting in carboxylic acid functions. The structure reveals the alternate arrangement of two square planar and two octahedral $Ni(II)$ centers located at four corners of the diamond core. The square planar $Ni1$ and $Ni3$ are in $\{N_3O\}$ coordination environment and the octahedral $Ni2$ and $Ni4$ are in N_2O_4 coordination environment. The square planar $Ni1$ and $Ni3$ are bound to the N_3 coordination pocket of each ligand, with an additional oxygen atom from the terminal carboxylate

Figure 2. Structural representation of complex **2** (left) and its core structure (right).

Figure 3. Structural representation of complex **3** (left) and its core structure (right).

function. The four Ni(II) ions in the tetranuclear core are linked together by diazine N–N bridges resulting in a diamond-shaped cyclic ring. Both the ligands coordinates in an asymmetric mode with twisted conformation around diazine N–N bond.

Each ligand bears two negative charges, ensuring the charge balance by the presence of four methoxy anions bound to octahedral nickel centers. The distance between the adjacent Ni(II) centers fall in the range 4.33–4.73 Å. The metal–ligand (M–L) bond distances fall in the range 1.82–1.90 Å for square planar Ni1 and Ni3, and 2.01–2.20 Å for octahedral Ni2 and Ni4. The short in plane M–L distances of Ni1 and Ni3 are in consistence with the low spin electronic state of the metal centers.

3.3 Description of Crystal Structure of $[Cu_4(L^{2b})_2(OTf)_4(H_2O)_4] \cdot 6H_2O$ (**3**)

The structural representation of complex **3** is shown Figure 3, and important metrical parameters are listed in Table 1. The crystal structure reveals a tetranuclear arrangement of four copper (II) ions, in which two distorted octahedral copper centres are each bound to a hydrolysed ligand fragment (Figure 3), where hydrolysis has occurred at one of the hydrazone imine carbon site, leading to a terminal hydrazine group. Each ligand acting in a twisted heptadentate manner and bridging the metals with a tridentate and bidentate end. The two mononuclear (Cu1) end fragments are connected through a central, square pyramidal, five-coordinate

copper ion (Cu2), positioned at an inversion centre. Each hydrolysed ligand bears two negative charges, the overall charge is balanced by the presence of four triflate ions coordinated to two mononuclear copper (II) metal centres. Protons on N(2) and N(5) were located in difference fourier map indicating the dianionic nature of the ligand. The ligand's cis conformation creates a flat $\{N_3O\}$ coordination environment in the plane and the axial positions are occupied by two coordinated triflate ions resulting in a distorted octahedral geometry of the mononuclear copper fragment [Cu(1)]. The bridging copper, Cu(2), is externally bound to the two mononuclear fragments by diazine nitrogen N(5), carbonyl oxygen O(4) and carboxylate oxygen O(1) from its counter mononuclear unit. Two additional water molecules are coordinated to the central copper ion, one in axial position and other in equatorial position, resulting in a square pyramidal geometry. Cu–Cu distance between Cu1 and Cu2 is 4.70 Å.

3.4 Magnetic Properties

Variable-temperature magnetic data were collected for complex **1** and complex **3** in a 0.5 T field in the temperature range 2–300 K. The magnetic data for complex **1** is reported in Figure 4 (left) as $\chi_m T$ vs T plot. The drop in the $\chi_m T$ from 5.74 cm³ K mol^{−1} at 300 K to 0.10 cm³ K mol^{−1} at 2 K indicates the presence of intramolecular antiferromagnetic exchange coupling. No distinct maximum was observed in the $\chi_m T$ profile, but the drop in $\chi_m T$ value upon lowering the

Figure 4. Variable-temperature magnetism for complex **1** (left) and **3** (right) plotted as $\chi_m T$ vs T .

temperature clearly indicates the presence of dominant intramolecular antiferromagnetic exchange.

Magnetic data for complex **3** shows a similar profile, and it is reported in Figure 4 (right) as $\chi_m T$ vs T plot. The drop in the $\chi_m T$ from $1.34 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K to $0.16 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K indicates the presence of intramolecular antiferromagnetic exchange coupling. The $\chi_m T$ value $1.34 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature is consistent with the presence of four magnetically non-interacting copper(II) ions. The magnetic properties of the complex **2** are already reported²⁶ which shows the dominant antiferromagnetic interaction between Ni centres.

4. Conclusions

Linear polytopic ligands H_2L^1 and H_2L^2 have specifically encoded coordination information, and are able to strongly influence the self-assembly outcome to produce ordered $[n \times n]$ grid architectures. Coordination chemistry of these tritopic ligands with central pyridine framework has been investigated. Carboxylate groups have also been incorporated at the terminal position of the ligand backbone with an intention of extending grid assembly through inter-grid linkages. The balance between the donor characteristics of the ligand coordination pockets and metal-ion geometric preferences are clearly critical to the reaction outcome, but competition from other ligands (solvent molecules and counter ions) lead to unexpected oligonuclear products in preference to the anticipated grid architectures. In the present report we have described some nongrid tetranuclear complexes $\{[\text{Cu}_4(\text{H}_2\text{L}^{1b})_2(\text{OTf})_4(\text{OH})_2(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}\}_n$ (**1**), $[\text{Ni}_4(\text{L}^{2a})_2(\text{OCH}_3)_4] \cdot 4\text{H}_2\text{O}$ (**2**) and $[\text{Cu}_4(\text{L}^{2b})_2(\text{OTf})_4(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ (**3**) synthesized from tritopic ligands

starting with nickel(II) and copper(II) salts. These complexes have been identified by the use of X-ray crystal structural analyses to determine product identity. Both the tetranuclear copper clusters have shown the intramolecular antiferromagnetic exchange coupling. These results emphasize the fact that one might end up to oligomeric structures by self-assembly rather than the grid molecules.

Supplementary Information (SI)

CCDC-1817332-1817334 contain the X-ray crystallographic details in CIF format. IR spectra for complexes **1–3** are available as Supplementary Information at www.ias.ac.in/chemsci.

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