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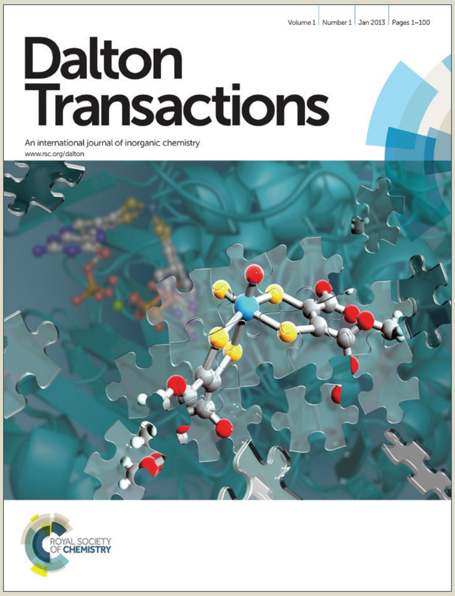

ROYAL SOCIETY OF CHEMISTRY

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Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Novel Cu^{II}-M^{II}-Cu^{II} (M = Cu or Ni) trinuclear and $[Na^{I}_{2}Cu^{II}_{6}]$ hexanuclear complexes assembled by bi-compartmental ligands: syntheses, structures, magnetic and catalytic studies†

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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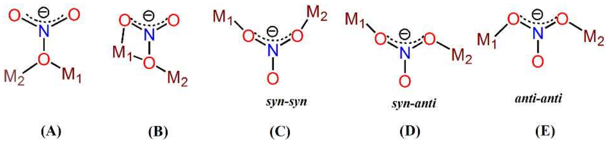
In the present work, two compartmental ligands H_2L^1 and H_2L^2 were in-situ generated during the syntheses of new trinuclear complexes, $[Cu_2Ni(L^1)(2,2'\text{-bpy})_2(NO_3)_2][ClO_4]_2$ (**5**), $[Cu_3(L^2)(NO_3)_2][ClO_4]_2$ (**6**), and $[Cu_3(L^2)(NCS)_2(NO_3)]^+$ that co-crystallizes in **7** with an $[Cu_6(L^2)_2Na_2(NO_3)_6(NCS)_4]$ unit to give a final molecular formula $[Cu_6(L^2)_2Na_2(NO_3)_6(NCS)_4][Cu_3(L^2)(NCS)_2(NO_3)]_2(NO_3)_2.5H_2O$(**7**). The magnetic property studies of **5**-**7** revealed weak Cu^{II}-Cu^{II} ferromagnetic interactions in compound **6** ($J_{Cu\text{-}Cu}/k_B$ = +1.4(1) K) and **7** ($J_{Cu\text{-}Cu}/k_B$ = +1.6 while intrinuclear Cu^{II}-Ni^{II}-Cu^{II} compound **5**, the magnetic coupling between two Cu^{II} ions is switched off by the diamagnetic square planar Ni^{II} bridge. The catalytic epoxidation of two olefins, namely styrene and cyclooctene, by *tert*-BuOOH (TBHP) were also explored in presence of a catalytic amount of **5**, **6** or **7** in MeCN. For styrene oxidation, **5** exhibited ~57% styrene epoxide selectively (conversion ~37%) with a TON of about 925 along with benzaldehyde (~43%), whereas **6** exhibited conversion up to ~63% (TON ~ 1575) with a good selectivity towards epoxide (~71%). For compound **7**, this conversion is more important (TON ~ 8108) probably due to the presence of more active sites involved in the epoxidation. The concerted path was found to be operative for styrene oxidation while a radical path for the oxidation of cyclooctene.

Introduction

In natural metalloproteins, metal ions are simultaneously assembled to form effective catalytic systems. These natural systems inspire chemists to expand the area of coordination chemistry and catalysis.[1] For example, ascorbate oxidase, laccase, ceruplasmin, particulate methane monooxygenase (*pMMO*) and others contain unique μ-OH trinuclear copper(II) complexes which were structurally modelled by using synthetic N or O ligands.[2] The functional models of these enzymes were developed by Stack, Pombeiro and others demonstrating the ability of tri- and poly-nuclear copper moieties to oxidise C–H bonds.[3] These works extensively demonstrated the importance of C–H bond oxidation by polynuclear complexes mimicking multicopper oxidases. Copper species are widely found in nature as di-, tri- or poly-nuclear species that catalyze selectively various oxidation reactions.[4] Although increasing attention has been paid to the design of Cu complexes with polydentate ligands as models of copper oxidases[4,5] and some mononuclear compounds have been recognized as catalysts for alkane oxidation,[6] the use of multicopper complexes for such reactions still remains an unexplored area of research. Our main aims are to find a simple synthetic method to generate multinuclear copper complexes with N, O-polydentate ligands and to investigate the catalytic activity of these complexes for the oxidation of alkanes under mild conditions, thus extending our interest of alkene functionalization.

The incorporation of main group elements like alkali metal ions in the transition metal complexes to get transition/non-transition metal ion assemblies is also an important field of research, as these may help to trap water into the crystal lattice to increase the water solubility of the final assemblies. In addition, the presence of nitrate ions in the molecular assembly may also be useful for *in vivo* generation of nitric oxide (NO) and other reactive nitrogen oxides that clearly have robust NO-like effects for humans, including blood pressure reduction, inhibition of platelet aggregation, and vasoprotective activity.[7] Apart from the ability to saturate free coordination sites as a monodentate or chelating ligand, NO_3^- can function as a bridge between copper and sodium ions within one-, two- or three-dimensional extended coordination networks. Most important bridging modes of NO_3^- that are observed in the literature have been denoted as $\mu_{1,1}$ (A),[8] $\mu_{1,1,2}$; (B),[8] *syn–syn*$\mu_{-1,2}$; (C),[9] *syn–anti* $\mu_{-1,2}$; (D)[10] and *anti–anti* $\mu_{-1,2}$; (E)[11][A–Ein **Scheme 1**]. The compound **7** contains a rare example of interesting $[Na_2Cu_6]$ metal/alkali metal based complexes as only two examples of such type of complexes with a $[NaCu_4]$ moiety are reported from an alkali template assembly of two end-on azido bridged dinuclear copper unit.[12,13]



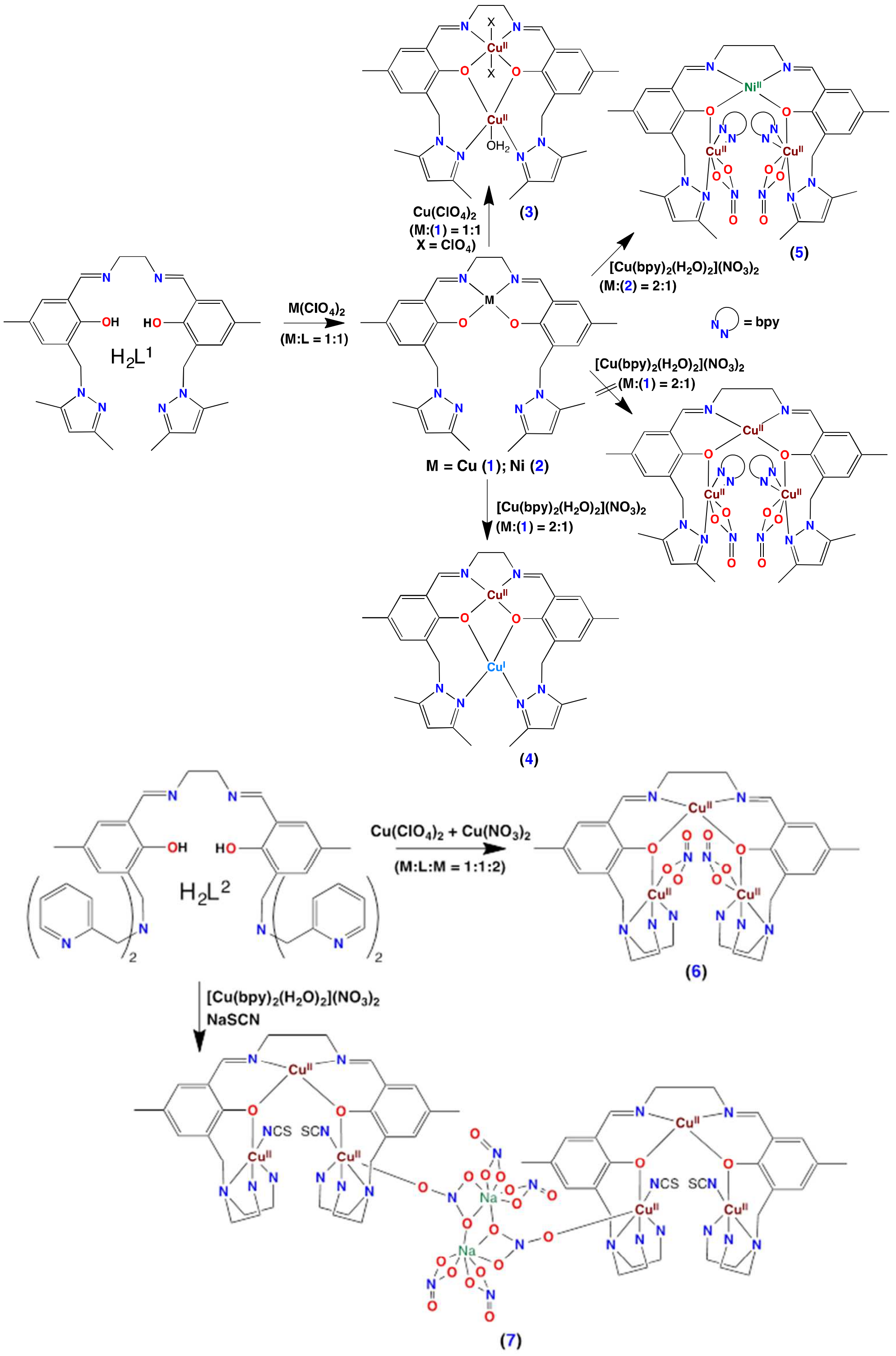
Scheme 1

Previously we reported the synthesis and characterization of mononuclear (L^1Cu^{II} (**1**)) and di-nuclear $L^1Cu^{II}_2$ (**3**), $L^1Cu^{II}Cu^{I}$ (**4**) complexes using a multidentate (N_4O_2) compartmental ligand (H_2L^1) (**Scheme 2**).[14,15] Herein, we report the synthesis, structural characterization and magnetic studies of a heterotrinuclear $[Ni^{II}Cu^{II}_2]$ complex (**5**), a trinuclear $[Cu^{II}_3]$ complex (**6**) and an octanuclear transition metal/alkali metal complex $[Cu_6(L^2)_2Na_2(NO_3)_6(NCS)_4][Cu_3(L^2)(NCS)_2(NO_3)]_2(NO_3)_2.5H_2O$(**7**). Furthermore, we have also tested all these complexes for epoxidation of olefins namely styrene and cyclooctene using *tert*-Butyl hydroperoxide (*t*-BuOOH) as terminal oxidant and also explored the magnetic interactions between the Cu^{II}centres of these metal ion complexes.

Results and discussion

Synthesis and Structural description of the complexes.
The hetero-trinuclear complex ($L^1Cu^{II}Ni^{II}Cu^{II}$) (**5**) was derived from its mononuclear analogue (L^1Ni^{II}) (**2**) of Schiff-base ligand (H_2L^1) while homo-trinuclear complex ($L^2Cu^{II}_3$) (**6**) was synthesized from the reaction of Schiff-base ligand (H_2L^2) with metal ion precursor $Cu(ClO_4)_2$ and $Cu(NO_3)_2$ in 1:1:2 ratio. Complex $[Cu_6(L^2)_2Na_2(NO_3)_6(NCS)_4][Cu_3(L^2)(NCS)_2(NO_3)]_2(NO_3)_2.5H_2O$(**7**) was prepared by reacting the Schiff-base ligand (H_2L^2) and metal ion precursor $[Cu(bpy)(H_2O)_2](NO_3)_2$ in presence of NaSCN.

Single crystal X-ray diffraction data reveals that **5** is a hetero-trinuclear Cu(II)-Ni(II)-Cu(II) species crystallizing in the P2/c monoclinic space group. In **5**, the coordination environments around the centrosymmetrical Cu(II)-Ni(II)-Cu(II) core are shown in **Fig. 1**. The $[L^1]^{2-}$ ligand coordinates to two Cu(II) metal ions that sandwich a central Ni ion. The two Cu(II) sites are symmetry related.
Each Cu(II) ion is coordinated by N_3O_3 donor set of atoms out of which O4(phenoxido) and N4 (3,5-dimethylpyrazole) from the parent ligand $[L^1]^{2-}$, N1 and N2 from bipyridyl ligand and O1 and O3 from the nitrate ion resulting a distorted octahedral geometry. The N1, N2, N4 and O1 atoms constitute the equatorial plane while O3 and O4 occupy the axial Cu(II) sites. On the other hand, the central Ni(II) ion is coordinated by a N_2O_2 donor set of atoms from the parent ligand.



Scheme 2. Scemetic presentation of synthesis of complexes.

The two N atoms are from imine part (N5 and its symmetry equivalent counterpart) and two O-atoms (O4 and its symmetry equivalent counterpart) from phenoxido group of $[L^1]^{2-}$, to form a square planar coordination sphere around the Ni1 metal ion. The phenoxido O-atoms are μ-bridging type and simultaneously coordinated to Cu1 and Ni1 atoms. There are two perchlorate anions in the outer coordination sphere to balance the total charge. The Cu1-Nx distances (x = 1, 2 and 4) are ~2.002, 2.009, and 1.996 Å, respectively while Cu1-Ox (x = 1, 3 and 4) lie in the 1.976 and 2.689 Å range which clearly indicate that the two Cu1 atoms are in highly distorted octahedral geometry. The square planar Ni1 metal ion fits well into the ligand cavity with short Ni-O bond distances of Ni-O4 ~1.857 Å and (**Table S1**) Ni-N5 ~1.853 Å.

The single crystal X-ray diffraction analysis indicated that **6** is a homo-trinuclear Cu(II)-Cu(II)-Cu(II) complex with two perchlorate anions to balance the charge. It crystallizes in the monoclinic *C2/c* space group. In complex **6**, the coordination environment around Cu(II)-Cu(II)-Cu(II) are shown in **Fig. 2** where two terminal Cu(II) (Cu2 and Cu3) metal ions sandwich the central Cu(II) site (Cu1) as observed in complex **5** with only differences being that the 3,5-dimethyl pyrazole in H_2L^1 is replaced by *N,N*-bis(2-methylpyridyl) group in H_2L^2.

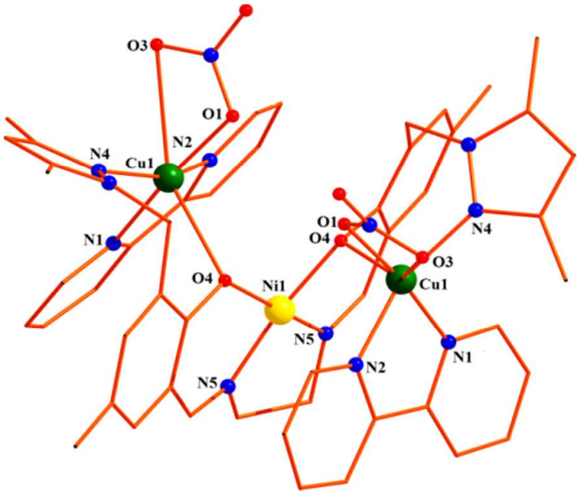


Fig. 1. Molecular view of **5** with coordination atom numbering scheme. Colour scheme: Green: Cu; Red: O; Blue: N; Yellow: Ni; Orange: C. All H-atoms and ClO_4^- are omitted for clarity.

In **6**, all the Cu(II) ions are in distorted octahedral geometry. The two terminal Cu(II) (Cu2 and Cu3) metal ions are coordinated by N_3O_3 donor set of atoms from the $[L^2]^{2-}$ ligand along with two nitrato anions. The Cu2 is coordinated by three N atoms (N2, N3 and N4) from the *bis*-picolylamine, one phenoxo O atom (O1) and two O atoms (O3 and O4) from one nitrate anion and likewise Cu2^a(symmetry operator a = -x,y,1/2-z) is coordinated by three N atoms (N2^a, N3^a and N4^a) from the *bis*-picolylamine, one phenoxo O-atom (O1^a) and two O atoms (O3^a and O4^a) from one nitrate anion to form the distorted octahedral geometry. On the other hand, the central Cu(II) ion(Cu1) is coordinated by N_2O_4 donor set of atoms O1 and O1^a from two phenoxido groups, O4 and O4^a from $\mu_{1,1,2}$-NO_3^- ion and N1 and N1^a from the ligand $[L^2]^{2-}$.

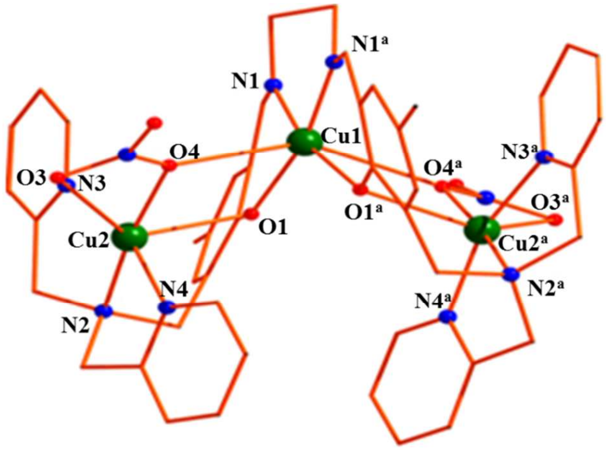


Fig. 2. Molecular view of **6** with coordination atom numbering scheme. Colour scheme: Green: Cu; Red: O; Blue: N; Orange: C. All H-atoms are omitted for clarity. a = -x,y,1/2-z.

The two phenoxido O-atoms (O1 and O1^a) and two O atoms (O4 and O4^a) from two NO_3^- ions are μ-bridging type. The geometries around the two terminal Cu metal ions (Cu2 and Cu2^a) are comparable. The Cu2-Nx distances (x = 2, 3 and 4; **Table S2**) are in the 1.919 to 2.025 Å range while Cu2-Ox distances (x = 1, 3 and 4) fall between 1.970 and 2.776 Å. The bond distances around the central Cu1 are: Cu1-Nx (x = 1 and 1^a) ~ 1.927Å and Cu1-Ox (x = 1, 1^a, 4 and 4^a) ~1.961-2.600 Å.

The structure of complex **7** (**Fig. 3**) showed that the two trinuclear $[Cu_3(L^2)(NCS)_2]$ moieties are connected by a $[Na_2(\mu_{1,2}\text{-}NO_3)_4\{\eta^2\text{-}(\mu_{1,2,3,3}\text{-}NO_3)_2]$ moiety almost in a linear fashion by two bridging NO_3^- group in a η^3-μ_3-NO_3 mode along with a co-crystallized $[Cu_3(L^2)(NCS)_2(NO_3)]^+$ cation. One non-coordinated nitrate ion is present in the crystal lattice to balance the overall charge. In the $[Cu_6(L^2)_2Na_2(NO_3)_6(NCS)_4]$ assembly the $[Cu_3]$ trinuclear unit is comprised of three Cu atoms Cu1, Cu2 and Cu3 in three different coordination environments. Cu1 is in octahedral ligand field coordinated by N1, N2, N3 and N9 and lie in the basal plane formed by *bis*-picolyl unit (N1, N2, N3) and one thiocyanate (N9) unit, whereas the axial positions are occupied by O1 (phenoxo) and O16 (NO_3^-). The central Cu2 atom is in square planar geometry coordinated by N4, N5 (imino), O1 and O2 (phenoxido) coming from the $[L^2]^{2-}$ ligand. Lastly, the terminal Cu3 metal ion is in square pyramidal geometry, the equatorial plane being occupied by N6, N7, N8 (*bis*-picolyl amine) and N10 (thiocyanate) atoms. The sole axial position is occupied by O2 (phenoxo) atom. The central sodium unit consists of two Na^+ ions in hepta-coordinating (O_7) ligand field with four μ-NO_3 ions mutually connecting two Na^+ions. In addition, there are two η^2,μ_3-NO_3 groups connecting two Na^+ ions along with Cu1 of the suitably faced Cu_3trinuclear units in a topology similar to that is observed in $[Na_2Cu_4(bemp)_2(OH)_2(NO_3)_2(OH_2)_4]\cdot 5H_2O$ (**1**$\cdot 5H_2O$; H_3bemp: 2,6-bis-[(2-hydroxyethylimino)-methyl]-4-methyl-phenol).[16] In the co-crystallized $[Cu_3(L^2)(NCS)_2(NO_3)]^+$ cation, the three Cu(II) metal ions, Cu4, Cu5 and Cu6, have a coordination environment similar to those observed in the $[Cu_3(L^2)(NCS)_2]$ part of the $[Na_2Cu_6]$ complex and compared well as Cu1≅Cu4, Cu2≅Cu5 and Cu3≅Cu6. Here the Cu4 differs from Cu1 only from the fact that the NO_3^- anion is terminal in nature instead of being additionally coordinated to two Na^+ ions as in $[Na_2Cu_6]$ complex. All the important bond lengths and bond angles are reported in **Table 1** and compared to the values commonly observed for such types of coordination species.[17-19]

Table 1 Selected Bond lengths (Å) and bond angles (º) of **7**

Bond length(Å)		O14 -Na1 -O15	52.1(2)
Cu1 -O1	2.389(6)	N12 -Cu4 -N20	97.7(3)
Cu6 -N16	1.984(7)	O1 -Cu2 -N4	92.6(3)
Cu1 -O16	2.582(8)	N13 -Cu4 -N20	173.6(3)
Cu6 -N17	2.030(6)	O1 -Cu2 -N5	159.5(3)
Cu1 -N1	1.984(8)	O3 -Cu4 -O5	171.6(3)
Cu6 -N18	1.997(8)	O1 -Cu2 -N9	78.1(2)
Cu1 -N2	2.056(8)	O3 -Cu4 -N11	91.1(3)
Cu6 -N19	1.954(8)	O2 -Cu2 -N4	158.6(3)
Cu1 -N3	1.955(9)	O3 -Cu4 -N12	98.9(3)
Cu1 -N9	1.949(8)	O2 -Cu2 -N5	93.2(3)
Cu2 -O1	1.923(6)	O3 -Cu4 -N13	87.8(3)
Cu2 -O2	1.906(6)	O2 -Cu2 -N9	94.8(2)
Cu2 -N4	1.908(8)	O3 -Cu4 -N20	85.8(3)
Cu2 -N5	1.929(8)	N4 -Cu2 -N5	85.2(3)
Cu2 -N9	2.870(8)	N15 -Cu5 -N19	88.6(3)
Cu3 -O2	2.319(6)	N4 -Cu2 -N9	106.2(3)
Cu3 -N6	1.994(9)	N14 -Cu5 -N19	102.0(3)
Cu3 -N7	2.029(9)	N5 -Cu2 -N9	83.0(3)
Cu3 -N8	2.001(8)	N14 -Cu5 -N15	83.6(4)
Cu5 -O4	1.912(5)	O2 -Cu3 -N6	99.9(3)
Cu5 -O3	1.907(7)	O3 -Cu5 -O4	94.2(2)
Cu6 -O4	2.348(6)	O2 -Cu3 -N7	90.7(3)
Cu5 -N14	1.921(8)	O3 -Cu5 -N14	162.9(3)
Cu3 -N10	1.949(9)	O2 -Cu3 -N8	93.7(3)
Cu4 -N20	1.968(9)	O3 -Cu5 -N15	93.5(3)
Cu4 -N13	2.052(8)	O3 -Cu5 -N19	94.8(3)
Cu4 -O5	2.463(15)	O11 -Na1 -O14	149.0(4)
Cu4 -N11	1.983(8)	O4 -Cu5 -N14	93.2(3)
Cu4 -O3	2.463(7)	O4 -Cu5 -N15	163.5(3)
Cu4 -N12	1.985(8)	O4 -Cu5 -N19	76.2(2)
Cu5 -N15	1.926(8)	Cu1 -O1 -Cu2	103.4(2)
Cu5 -N19	2.863(8)	O4 -Cu6 -N18	91.4(3)
Na1 -O8	2.465(8)	Cu2 -O2 -Cu3	109.0(3)
Na1 -O10	2.462(9)	N11 -Cu4 -N13	83.2(3)
Na1 -O11	2.330(11)	N2 -Cu1 -N9	179.5(4)
Na1 -O14	2.500(8)	N11 -Cu4 -N20	97.5(4)
Na1 -O15	2.389(9)	N3 -Cu1 -N9	96.8(3)
Na1 -O14a	2.342(7)	N12 -Cu4 -N13	82.7(3)
Bond angles (°)		O1 -Cu2 -O2	96.1(2)
O1 -Cu1 -O16	172.8(2)	N16 -Cu6 -N17	83.7(3)
O2 -Cu3 -N10	91.5(3)	N16 -Cu6 -N18	162.0(3)
O1 -Cu1 -N1	91.6(3)	N16 -Cu6 -N19	96.7(3)
N6 -Cu3 -N7	83.3(3)	N17 -Cu6 -N18	83.6(3)
O1 -Cu1 -N2	89.6(3)	N17 -Cu6 -N19	179.4(3)
N6 -Cu3 -N8	161.2(4)	O4 -Cu6 -N17	90.0(2)
O1 -Cu1 -N3	97.1(3)	Na1 -O14 -Na1_a	96.6(3)
N6 -Cu3 -N10	95.9(4)	O16 -Cu1 -N1	81.9(3)
O1 -Cu1 -N9	90.9(3)	O4 -Cu6 -N16	101.2(3)
N7 -Cu3 -N8	83.7(4)	N18 -Cu6 -N19	96.1(3)
N7 -Cu3 -N10	177.7(4)	O8 -Na1 -O11	104.1(4)
O16 -Cu1 -N2	92.7(3)	O8 -Na1 -O14	90.9(3)
N8 -Cu3 -N10	96.6(4)	Cu4 -O3 -Cu5	111.3(3)
O16 -Cu1 -N3	89.9(3)	O8 -Na1 -O15	92.3(3)
O5 -Cu4 -N11	80.7(4)	O8 -Na1 -O14_a	133.5(3)
O16 -Cu1 -N9	86.8(3)	O10 -Na1 -O11	120.8(4)
O5 -Cu4 -N12	88.5(3)	O10 -Na1 -O14	89.8(3)
N1 -Cu1 -N2	83.6(3)	O8 -Na1 -O10	51.7(3)
O5 -Cu4 -N13	89.1(4)	O11 -Na1 -O14_a	104.0(4)
N1 -Cu1 -N3	164.1(3)	O14 -Na1 -O14_a	83.4(3)
O5 -Cu4 -N20	97.3(4)	O14_a -Na1 -O15	118.3(3)
N1 -Cu1 -N9	96.4(3)	O11 -Na1 -O15	99.6(4)
N11 -Cu4 -N12	162.3(4)	O10 -Na1 -O15	129.5(3)
N2 -Cu1 -N3	83.2(3)	O10 -Na1 -O14a	82.1(3)

Symmetry operators: x,y,z; -x,-y,-z.

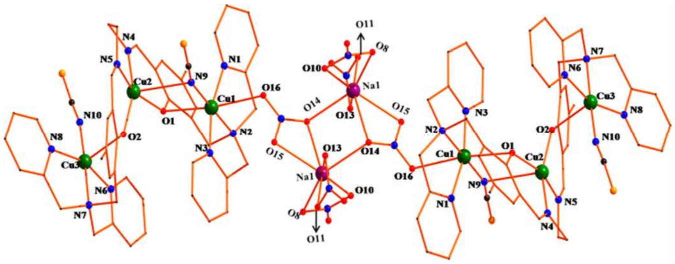


Fig. 3. (a) Molecular view of **7** with colour scheme: Green: Cu, Red: O, Blue: N, Yellow: S, Violet: Na, Orange: C atoms. All H-atoms, Nitrate counter anion, one trinuclear unit and water of crystallization are omitted for clarity.

The Cu1-N9 (NCS) and Cu2-N9 distances are found to be 1.950 and 2.870 Å, respectively indicating a discrete Cu1-N9 bond while only a Cu2-N9 semi-bond is observed. Nevertheless the NCS ligand can be considered as a bridging ligand as also observed for the co-crystallizing $[Cu_3(L^2)(NCS)_2(NO_3)]^+$cation with Cu6-N18 = 1.954 Å and Cu5-N18 = 2.862 Å. The neighboring Cu···Cu separations in the trinuclear fragments fall in the 3.395-3.622 Å range, whereas the Na···Na distance is 3.612 Å.

UV-Vis spectroscopy

The electronic spectra of complexes **5-7** were recorded in MeCN (**Fig. 4**). The electronic transition band appears at 345 nm with a molar extinction coefficient (ε) 1.87 x 10^5 $dm^3mol^{-1}cm^{-1}$ for complex **5** corresponding to an ILCT/MLCT band. For complex **6**, bands are located at 633 and 364 nm with ε values of 302 and 1.9 x 10^5 $dm^3mol^{-1}cm^{-1}$ respectively while the corresponding bands for complex **7** appear at 604 and 360 nm with ε values of 894 and 2.3 x 10^5 $dm^3mol^{-1}cm^{-1}$ respectively. The bands at longer wavelengths may be attributed to the d-d transitions while bands at shorter wavelengths (345, 360 and 364 nm) are due to intra-ligand or/and metal-ligand charge-transfer transitions.

Magnetic properties

The temperature dependence of magnetic susceptibility for complexes **5-7** have been measured at 1000 Oe between 1.8 and 290 K (**Fig. 5**). Considering the symmetry in the crystal structure of **7**, the magnetic data are normalized for six Cu^{II} centers with two different trinuclear Cu^{II}-Cu^{II}-Cu^{II} fragments while for **5** and **6**, the magnetic data are normalized per two and three Cu(II) sites respectively. At room temperature, the χT product of **5** is 0.90 cm^3K/mol. This value does not change with lowering of the temperature indicating the Curie-type paramagnetism of complex **5**. The $3d^8$ square planar Ni^{II}center is as expected diamagnetic and provide a good isolation of the two paramagnetic Cu^{II} sites. The χT product of 0.90 cm^3K/mol is thus the simple sum of the Curie contributions from the two $S = ½$ Cu^{II} centers with a g factor of about 2.2(1). The two Cu^{II} centers are quite well separated from each other in the crystal structure and thus no significant inter-molecular short-contacts are observed. Accordingly, the field dependence of the magnetization (**Fig. S1**) exhibits a saturation at 1.83 K under 7 T for which it reaches 2.27 μ_B as expected for two isolated $S = ½$ spins. The fit of M *vs* H/T data at 1.83 K (**Fig. S1**) as a sum of two $S = ½$ Brillouin functions works perfectly well and allows an estimation of the g factor around 2.24(6) for the Cu^{II} centers consistently with the g value evaluated from the Curie constant (*vide supra*).

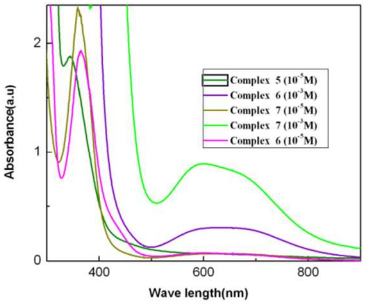


Fig. 4. UV-Vis spectra of complexes **5**, **6** and **7** in MeCN. [c] = 1.0 x 10^{-3} M for d-d bands at longer wavelengths and [c] = 1.0 x 10^{-5} M for ILCT/MLCT bands at shorter wavelengths.

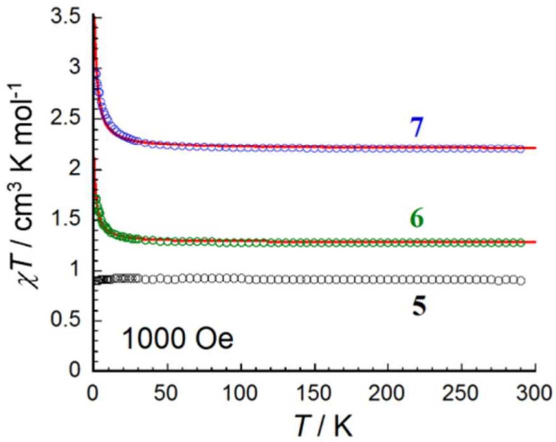
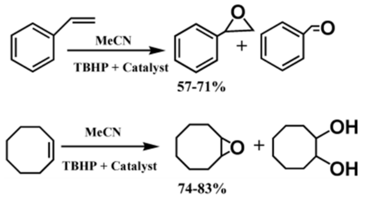


Fig. 5. The χT vs T plots of complexes **5-7** between 1.8 and 290 K at 1000 Oe (with χ defined as the magnetic susceptibility equal to M/H per mole of complex). The hollow circles are the experimental data and the red solid lines are the best fit of the experimental data for **6** and **7** as described in text.

Both complexes **6** and **7** consist of trinuclear Cu^{II}-Cu^{II}-Cu^{II} species and their corresponding χT products at 290 K, 1.28 and 2.20 cm^3K/mol for **6** and **7** respectively, are in agreement with three (for **6**) and six (for **7**) Cu^{II} magnetic centers respectively with average g values of 2.1(1) for **6** and 2.0(1) for **7**. With lowering of temperature, both χT products remain almost the same until about 30 K and then increases to reach 1.72 and 2.96 cm^3K/mol at 1.8 K for **6** and **7** respectively. This thermal behavior indicates without ambiguity the presence of ferromagnetic interactions in both complexes between the Cu^{II}centers of the trinuclear species. In order to probe the exchange between the $S = ½$ Cu^{II} sites, the magnetic coupling between the two terminal Cu^{II} spins and the central Cu^{II} one are considered, as a first approximation, to be the same in all the trinuclear moieties. A low-field analytical expression of the magnetic susceptibility of **6** and **7** have been deduced from the following Heisenberg spin Hamiltonian: $\boldsymbol{H} = -2J(\boldsymbol{S}_{Cu1}\bullet\boldsymbol{S}_{Cu2}+\boldsymbol{S}_{Cu2}\bullet\boldsymbol{S}_{Cu3})$ where J is the average Cu^{II}-Cu^{II} coupling. This simple model reproduce perfectly the experimental χT vs T data at 1000 Oe (solid red lines in **Fig. 5**) with the following sets of parameters: $J/k_B = +1.4(1)$ K with $g = 2.1(1)$ for **6** and $J/k_B = +1.6(3)$ K with $g = 2.0(1)$ for **7**. In addition, the field dependence of the magnetization of **6** and **7** were also collected in the 1.8 – 8 K range (**Fig. S2**). At 7 T and 1.83 K, the magnetization saturates at 3.25 μ_B for **6** which is expected for three $S = ½$ spins or an $S_T = 3/2$ spin system ($g_{av} = 2.17(5)$), and it saturates near 5.70 μ_B for **7** consistent with six $S = ½$ spins or two $S_T = 3/2$ spin systems ($g_{av} = 1.90(5)$).

Catalytic activities

In the present report we have explored the catalytic epoxidation of two olefins, namely styrene and cyclooctene by *t*-BuOOH in presence of a catalytic amount of Schiff-base complexes **5**, **6** and **7** in MeCN. The results of the catalytic oxidation of different substrates are given in **Table 2**and shown in **Scheme 3**. Using complex **5** as catalyst, under homogeneous conditions, the styrene oxidation with *t*-BuOOH gives ~57% styrene epoxide selectively (conversion ~37%) with a TON ~925 (TONs: turn over numbers = moles of substrate converted per mole of Cu) (**Table 2**) along with a moderate amount of benzaldehyde (~45%). Besides, the corresponding conversion using the complex **6** increases to ~63% (TON ~ 1575) with a good selectivity towards epoxide (~71%) while for complex **7**, the conversion became much more efficient and the corresponding TON reaches ~8108; likely because of the presence of more active sites in **7** involved during the transformation to epoxide. When cyclooctene is used as substrate, complex **6** exhibits an excellent conversion of ~71% (**Table 2**) with ~78% selectivity for cyclooctene oxide. Apart from cyclooctene oxide, cyclooctane-1,2-diol (~15%) was also generated owing to hydrolysis of the epoxide. When complex **5** is used, the conversion drastically falls down to ~46% with epoxide selectivity of ~74%; on the other hand in case of complex **7** a significant increase in % conversion, selectivity and TON is observed.



Scheme 3

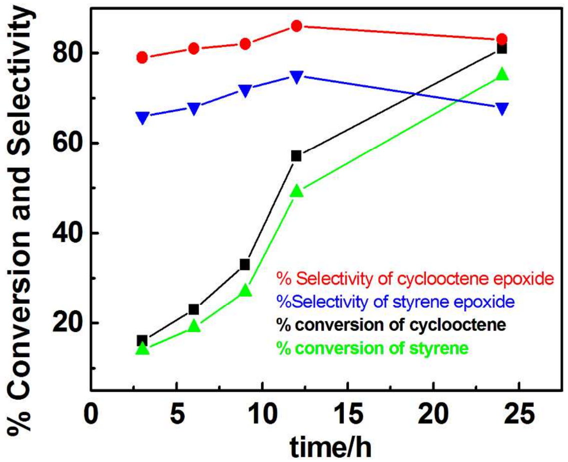


Fig. 6. **%**Conversions of styrene and cyclooctene at different reaction times in liquid phase partial oxidation by **7.**

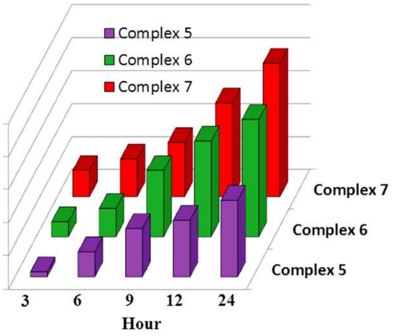


Fig. 7. Comparison of styrene conversion at different reaction times in liquid phase partial oxidation by **5, 6** and **7**.

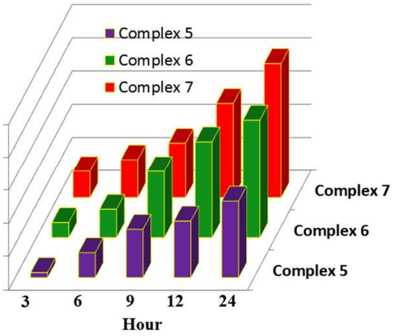


Fig. 8. Comparison of cyclooctene conversion at different reaction time in liquid phase partial oxidation by **5, 6** and **7.**

Table 2. Homogeneous catalytic epoxidation[a] of olefins by *t*-BuOOHcatalysed by compounds **5-7** in MeCN, [Substrate] = 50 mmol, temperature 55 °C

Catalyst	Substrate	Reaction time (h)	Conversion	% yield of products		TON[b](TOF)[c]
				Epoxide	Others	
5 21mg (0.016 mmol)	Styrene	3	3	36	64	
		6	13	54	46	
		9	24	59	41	
		12	29	61	39	
		24	37	57	43	925(75)
	Cyclooctene	3	5	70	30	
		6	15	72	28	
		9	29	75	25	
		12	34	78	22	
		24	46	74	26	1150(88)
6 21 mg (0.017 mmol)	Styrene	3	8	70	30	
		6	15	73	27	
		9	36	76	24	
		12	49	74	26	
		24	63	71	29	1575 (120)
	Cyclooctene	3	9	77	23	
		6	17	79	21	
		9	40	81	19	
		12	58	84	16	
		24	71	78	22	1775 (142)
7 18 mg (0.0037 mmol)	Styrene	3	14	66	34	
		6	19	68	32	
		9	27	72	28	
		12	49	75	25	
		24	75	68	32	8108 (552)
	Cyclooctene	3	16	79	21	
		6	23	81	19	
		9	33	82	18	
		12	57	86	14	
		24	81	83	17	8756 (642)

[a]Solvent: CH_3CN; temperature: 60°C.[b]TON: turn over number = moles of substrate converted per mole of Cu. [c]TOF: turnover frequency = moles of substrate converted per mole of Cu center per hour measured in 12 hours.

Table 3. Comparison of the catalytic efficiency of **5**, **6** and **7** with other reported copper(II) catalysts for the styrene epoxidation with t-BuOOH in MeCN in 24 hours.

Catalyst	Conversion (%)	Epoxide selectivity(%)	TON [TOF]	Ref.
$[Cu(L^1)(H_2O)](ClO_4)$	86	42	[69]	4(k)
$[Cu(L^2)]$	75	54	[60]	4(k)
$[Cu(L^3)]$	99	39	[79]	4(k)
$[Cu(HL^1)(NO_3)]_n$	100	86	[252]	4(l)
$\{[Mg(H_2O)_6][Cu(pydca)_2].2H_2O\}_n$	100	58	[158]	4(l)
$[Cu_2L(\mu_{1,1}\text{-N3})(\mu_{1,3}\text{-N3})(\mu_{1,1,1}\text{-N3})]$	88	90	264	20
$[Cu_4(O)(L^1)_2(CH_3COO)_4]^a$	85	90	[4.2]	21
$[Cu_4(O)(L^2)_2(CH_3COO)_4].CH_3CN^a$	88	89	[4.4]	21
$[Cu_4(O)(L^3)_2(CH_3COO)_4]^a$	83	88	[4.1]	21
$[Cu_4(O)(L^4)_2(CH_3COO)_4]^a$	81	92	[4]	21
3	70	53	280	15
4	68	52	272	15
5	37	57	925[75]	This work
6	63	71	1575[120]	This work
7	75	68	8108[552]	This work

.[a] *H_2O_2 was used as terminal oxidant*

Fig. 6 displays the **%** conversions and epoxide selectivity of styrene and cyclooctene at different reaction times in liquid phase partial oxidation catalyzed by **7** whereas the relative efficiencies of the catalysts are given in **Fig. S3** for complex **5**and **Fig.S4** for complex **6.**

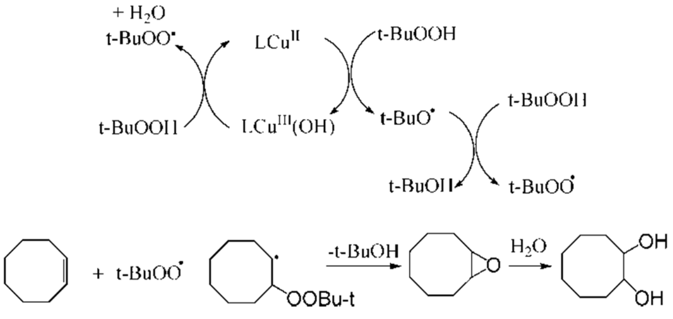
As observed from the results listed in **Table 2** and graphically presented in **Fig. 7** and **8**, the major products of the reactions are epoxides and the selectivity for these products are relatively high. The high TONs obtained for the substrates suggest a very good catalytic efficiency of these complexes in presence of *t*-BuOOH as oxidant. We have also calculated the turnover frequency (TOF) for the conversion of styrene/cyclooctene for the period of 12 hours where almost linear dependence of conversion with time is prevailing and found to be: 77/88, 120/142, 552/642 using complex **5**, **6**, **7** respectively. The huge difference of conversion during the epoxidation reactions catalyzed by **5**, **6** and **7** may be due to the different number of central metal ions present in the complexes. The large difference in catalytic efficiency between complexes **5** and **6** may be attributed to the fact that the Ni metal ion in complex **5** either remains silent or takes poorly part to the catalytic activity compare to the Cu metal ions in complex **6**. In this context, it may be mentioned here that [Ni(L^1)] does not show any catalytic effect on such epoxidation reactions.[20] In case of complex **7**, the large number of active centers compared to complex **5** and **6** is likely responsible for its enhanced catalytic efficiency. The order of catalytic efficiency follows the order **5<6<7** and may be attributed to the cooperative effect i.e., with the increase in catalytic site the efficiency increases. In case of styrene, the epoxide formed undergoes further oxidation to form benzaldehyde (~40%) with an equivalent amount of formaldehyde. The yield of CH_2O was measured by mixing equal volumes of the solutions to be analyzed and acetylacetone in an acetic acid–ammonium acetate buffer medium and measuring the absorbance at 410 nm and comparing it with the standard calibration curve constructed by reacting equal volumes of different known concentrations of CH_2O and acetylacetone under the similar reaction conditions.[21]

It is worth noting that a blank reaction of the oxidation of cyclooctene in the absence of any catalyst under identical reaction conditions showed very poor conversion (~ 8%) and epoxide selectivity, thereby confirming the catalytic role of the Cu complexes in these epoxidation reactions.

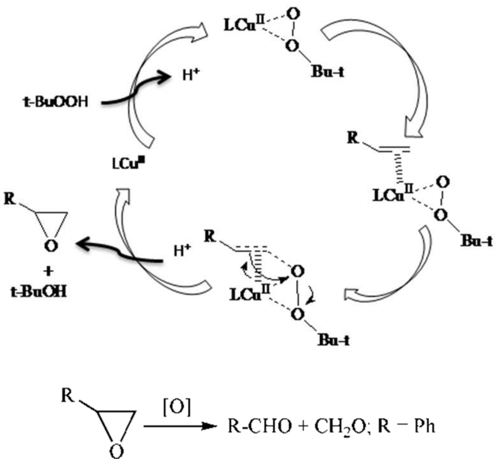
There are only few reports on the epoxidation of olefins catalyzed by polynuclear Cu(II)-Schiff base complexes where TONs were found to be in the 160-290 range[22]and TOFs were in 5-17 range for heterogeneous condition and 2.2-6.0 for homogeneous conditions[23]**(Table 3)**. To the best of our knowledge, our systems showed the highest TON/TOF values for Cu(II)-Schiff base complexes under homogeneous reaction conditions. In solution, the existence of trinuclear species for all the complexes **6** and **7** were confirmed by HRMS analysis (**Fig. S5**). However, in case of complex **5**, we failed to get the expected molecular ion peak even using very low cone potential. Rather **5** undergoes fragmentation to give ESI-MS^+(m/z) as: 569.2297([Ni(L^1)+H^+]); 280.9750 ([Cu(bpy)-(NO_3)]) (**Fig. S5**). It was also observed that the catalysts remain intact even after the completion of 2-3 catalytic cycles.

The epoxidation reactions are typically believed to operate either through a radical or concerted pathway.[24]In order to ascertain which one is operative, we decided to carry out epoxidations in the presence of potential radical scavengers like 2,4-di-*tert*-butylphenol.It was interesting to observe that the epoxidation reaction of cyclooctene was completely quenched while the reaction of styrene proceeds smoothly thereby convincingly suggesting a radical pathway for epoxidation of cyclooctene and a concerted pathway for styrene.[24]

According to the mechanistic proposal (**Scheme 4**) LCu^{II} (adopted to represent the catalyst in simple way) converts t-BuOOH into t-BuOO$^{\bullet}$ by two pathways. In the first pathway there occurs a reductive cleavage of the peroxide bond of t-BuOOH by LCu^{II} to form t-BuO$^{\bullet}$ and LCu^{III}(OH). The t-BuO$^{\bullet}$ in turn, rapidly abstracts a hydrogen atom from t-BuOOH to form more thermodynamically stable t-BuOO$^{\bullet}$.[25]Now one electron oxidation of t-BuOOH by LCu^{III}(OH) completes the catalytic cycle with the formation of the second t-BuOO$^{\bullet}$ and H_2O and regenerates LCu^{II}. Thus, in one complete catalytic cycle three mole of t-BuOOH are used up to generate one mole of t-BuOH, one mole of water, and two moles t-BuOO$^{\bullet}$. The t-BuOO$^{\bullet}$ radical thereby generated now reacts with cyclooctene to generate cyclooctene-oxide, which may undergo hydrolysis to form cyclooctane-1,2-diol as outlined in **Scheme 4a**.



Scheme 4a



Scheme 4b

A tentative concerted nechanism of the epoxidation of styrene can be framed as outlined in **Scheme 4b** for cyclooctene.As revealed from **Scheme 4b**, the catalysts, designated as LCu^{II}, takes up t-BuOOH to form LCu^{II}•••$OOBu^t$ adduct which further coordinates to styrene to bring the oxidant and the substrate closer to each other. Now this adducts leads to the formation of epoxide and regeneration of catalyst. The epoxide undergoes further oxidation to form benzaldehyde and formaldehyde.

Conclusion

Two compartmental ligands H_2L^1 and H_2L^2 were in-situ generated during the syntheses of three new trinuclear complexes: (i) a hetero-trinuclear complex (**5**) from a mononuclear complex $[L^1Ni^{II}]$ and $[Cu(2,2'\text{-}bpy)(H_2O)_2](NO_3)_2$, (ii) a homo-trinuclear complex $(L^2Cu^{II}_3)$ (**6**) from the reaction between H_2L^2 and a mixture of $Cu(ClO_4)_2$ and $Cu(NO_3)_2$ in 1:1:2 mole ratio and (iii) $[Cu_3(L^2)(NCS)_2(NO_3)]^+$ that co-crystallizes in **7** with an $[Cu_6(L^2)_2Na_2(NO_3)_6(NCS)_4]$ unit to give complex **7** $[Cu_6(L^2)_2Na_2(NO_3)_6(NCS)_4][Cu_3(L^2)(NCS)_2(NO_3)]_2(NO_3)_2.5H_2O$ obtained from H_2L^2 using $[Cu(bipy)(H_2O)_2](NO_3)_2$ and NaSCN. The trinuclear Cu(II)-Ni(II)-Cu(II) complex, **5**,contains a diamagnetic square planar Ni(II) metal ion that bridges and prevents the two terminal Cu(II) centers to interact magnetically. Therefore, this complex displays a Curie paramagnetism. On the other hand, the three $S = ½$ Cu(II) spin carriers in **6** are ferromagnetically coupled ($J/k_B = +1.4(1)$ K) leading to an $S_T = 3/2$ ground state for this complex. A Similar magnetic behavior is observed for complex **7** with an average Cu(II)-Cu(II) magnetic interaction of +1.6(3) K. The catalytic epoxidation of styrene and cyclooctene by *t*-BuOOH has been explored in presence of a catalytic amount of complexes **5**, **6** and **7** in MeCN. As far as we know, these complexes exhibit the highest TONs for epoxidation of olefins particularly in homogeneous liquid phase partial oxidation catalyzed by polynuclear Cu(II)-Schiff base complexes. The concerted path was found to be operative for styrene oxidation while a radical path for the oxidation of cyclooctene.

Experimental

Reagents

3,5-dimethylpyrazole, $[Cu(2,2'\text{-}bpy)(H_2O)_2](NO_3)_2$, 2-chloromethyl-6-carbaldehyde-4-methylphenol and 2-[*N,N*-*bis*(2-methylpyridyl)-aminomethyl]-6-carbaldehyde-4-methylphenol were prepared using reported methods.[15,26,27] $Cu(ClO_4)_2·6H_2O$ (Aldrich), $Cu(NO_3)_2·3H_2O$ (Aldrich), $Ni(ClO_4)_2·6H_2O$ (Aldrich), ethylenediamine (Merck, India), triethylamine (Et_3N) (Merck, India), *bis*-picolylamine (Aldrich), sodium thiocyanate (Merck, India), 2,4-di-*tert*-butylphenol(Aldrich),acetylacetone (Merck, India), ammonium acetate (Merck, India),*t*-BuOOH (Aldrich)are of reagent grade and used as received. Solvents like MeCN (Merck India),methanol, ethanol, THF and other solvents are of reagent grade and were dried by standard methods before use.

Physical measurements

Elemental analyses were carried out using a Perkin–Elmer 240 elemental analyzer. ^1H NMR were recorded in $CDCl_3$ on a Bruker 300 MHz NMR spectrophotometer using tetramethylsilane (δ = 0) as an internal standard. Electronic spectra were recorded on Agilent-8453 diode array UV–Vis spectrophotometer. Infrared spectra (400–4000 cm^{-1}) were recorded from KBr pellets on Nicolet Magna IR 750 series-II FTIR spectrophotometers. TOF-MS$^+$ spectra were generated on a waters HRMS instrument (model: XEVO G2QTOF).

Single crystal X-ray diffraction

Single crystal X-ray data of complexes **5-7** were collected on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated Mo $K_\alpha$radiation (λ= 0.71073 Å). Data collection, reduction, structure solution, and refinement were performed using the Bruker APEX-II suite (v2.0-2) program. All available reflections to $2\theta_{max}$ were harvested and corrected for Lorentz and polarization factors with Bruker SAINT plus. Reflections were then corrected for absorption; inter frame scaling, and other systematic errors with SADABS.[28]The structures were solved by the direct methods and refined by means of full matrix least-square technique based on F^2 with SHELX-97 software package.[29]All the hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms belonging to carbon and nitrogen atoms were placed in their geometrically idealized positions, while hydrogen atoms on oxygen atoms of coordinated water were found on the difference Fourier map, and all of them were constrained to ride on their parent atoms. Hydrogen atoms were assigned to ideal positions using the appropriate HFIX command in SHELXL-97. It is to be noted that the asymmetric unit of **7** contains two bipyridine molecules and they were not stable enough during refinement cycles, and thus all the positional parameters were fixed in space to make them reasonable. One of the bipy molecules is disordered over two positions along with a water molecule (O21) residing at an inversion center.Thus for a particular situation, in one set present in a unit cell, awater and a bipy molecule were present on either side of the inversion centre and they are engaged in hydrogen bonding. Furthermore, during the development of the structure it became apparent that U_{eq} values of some atoms of both the bipyridyl ligand in **7** were larger than usual and thus ADP restraints were also applied in order to make them acceptable. Furthermore, ADP restraints were applied on oxygen atoms of a coordinated nitrate ion to make them reasonable.Drawings of molecules were generated with the programs like DIAMOND-3.0, MERCURY-3.0 and PLATON. The crystallographic data for **5-7** are given in **Table 4**.

Magnetic measurements

The magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.85 and 300 K for *dc* applied fields ranging from -7 to 7 T. Measurements were performed on microcrystalline samples of 25.47 mg for **5**, 27.00 mg for **6** and 24.29 mg for **7**. The magnetic data were corrected for the sample holder and the diamagnetic contributions.

Experimental set up for catalytic oxidation

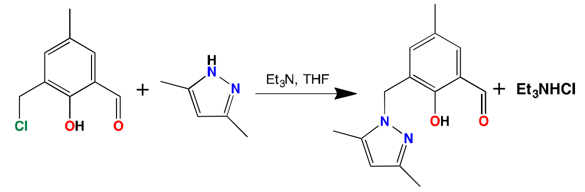
The catalytic epoxidation reactions were carried out in the liquid phase in a batch reactor at the desired temperature. Typically, a 50 mL two-neck round-bottomed flask equipped with a water condenser containing 50 mmol alkene in 10 mL acetonitrile (MeCN) solvent and 0.05 mmol of catalyst was kept in a pre-heated oil bath. 2 ml of *t*-BuOOH was then added to the mixture and was magnetically stirred continuously for 24 h. 0.5 mL of H_2O_2 was added intermittently at a time interval of 60 min. The products of the epoxidation reactions were collected at different time intervals and were identified and quantified by gas chromatography.

Table 4 Crystallographic data, details of data collection and structure refinement parameters for **5-7**

Complex	**5**	**6**	**7**
Formula	$C_{50}H_{50}Cl_2Cu_2NiN_{12}O_{16}$	$C_{44}H_{44}Cl_2Cu_3N_{10}O_{16}$	$C_{214}H_{210}Cu_{12}N_{56}Na_2O_{43}S_8$
Formula Weight	1331.71	1230.44	5302.32
Crystal System	Monoclinic	Monoclinic	Triclinic
Space group	P2/n (No. 13)	C2/c (No. 15)	P-1(No. 2)
a [Å]	14.7716(2)	26.9977(19)	12.2539(8)
b [Å]	9.4644(1)	12.3081(8)	18.6210(13)
c [Å]	19.5306(2)	15.3946(10)	27.0991(18)
α [°]	90	90	102.507(4)
β [°]	97.530(1)	95.984(5)	93.336(4)
γ [°]	90	90	108.678(4)
V [Å^3]	2706.92(5)	5087.6(6)	5664.2(7)
Z	2	4	1
D(calc) [g/cm^3]	1.634	1.606	1.554
μ(MoK$_\alpha$) [/mm]	1.304	1.427	1.266
F(000)	1364	2508	2711
Temperature (K)	293	273	100
θ Min-Max [º]	1.6, 27.5	1.5, 26.7	1.3, 24.6
Dataset	-19: 18 ; -12: 12 ; -25: 25	-34: 34 ; -15: 15 ; -19: 19	-14: 14 ; -21: 21 ; -31: 31
Tot., Uniq. Data, R(int)	40002, 6241, 0.046	36446, 5392, 0.107	46084, 19066, 0.068
Observed data [I > 2.0 σ(I)]	4547	2075	10719
N_{ref}, N_{par}	6241, 371	5392, 340	19066, 1418
R, wR$_2$, S	0.0515, 0.1668, 0.99	0.0575, 0.1947, 0.99	0.0848, 0.2330, 1.04

Synthesis of 2-formyl-4-methyl-6-(3,5-dimethyl-pyrazole)-phenol

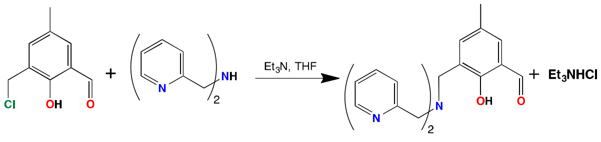
2-chloromethyl-6-carbaldehyde-4-methylphenol (1.515 g, 8.2 mmol) was dissolved in 15 ml dry THF in a round bottom flask. 3,5-dimethylpyrazole (0.7883 g, 8.2 mmol) and triethylamine (Et_3N) (1.659 g, 16.4 mmol) were dissolved in 10 ml dry THF and this mixture was added dropwise to the 2-chloromethyl-6-carbaldehyde-4-methylphenol solution. A rapid precipitation of Et_3NHCl was observed and the colour of the solution turned bright yellow (**Scheme 5**). After 24 hours of stirring, the precipitate was filtered and subsequently solvent (THF) was removed under reduced pressure to get an oily product that yielded a yellow crystalline solid after 2 days at 4°C. The solid product was then filtered and washed with cold ether. Yield 72%.^{1}H NMR (in $CDCl_3$, 300 MHz): δ in ppm 2.23-2.28 (9 H, m, -$ArCH_3$), 5.27 (2H, s, -CH_2), 7.09 (1H, s, -ArH), 7.27 (1H, s, -ArH), 7.28 (1H, s, -ArH), 9.88 (1H, s, -CHO), 11.23 (1H, brs, -ArOH).



Scheme 5

Synthesis of 2-(*N,N-bis*(2-methylpyridyl)amino-methyl)-6-carbaldehyde-4-methylphenol

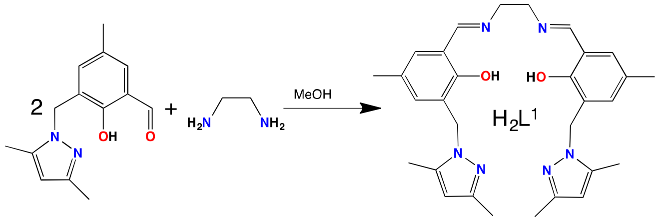
2-chloromethyl-6-carbaldehyde-4-methylphenol (1.515 g, 8.2 mmol) was dissolved in 15 ml dry THF in a round bottom flask. *Bis*-picolylamine (1.630 g, 8.2 mmol) and triethylamine (Et_3N) (1.659 g, 16.4 mmol) were dissolved in 10 ml dry THF and this mixture was added drop wise to the 2-chloromethyl-6-carbaldehyde-4-methylphenol solution. An instant precipitation of Et_3NHCl was observed and the colour of the solution turned to bright yellow (**Scheme 6**). After 24 hours of stirring, the precipitate was filtered off. Solvent (THF) was removed under reduced pressure to afford an oily product that yields a light yellow crystalline solid after 2 days at 4°C. The solid product was then filtered and washed with cold ether. Yield 78%.^{1}H NMR (in $CDCl_3$, 300 MHz): δ in ppm 2.27 (3H, s, -Me); 3.85 (2H, s, Ar-CH_2-N); 3.94 (4H, s, N-CH_2-py); 7.16-7.68 (10H, aromatic H); 8.57 (s, 1H, -CHO); 10.39 (s, 1H, -OH).



Scheme 6

Synthesis of $[Cu_2Ni(L^1)(2,2'\text{-bpy})_2(NO_3)_2].(ClO_4)_2$ (5).

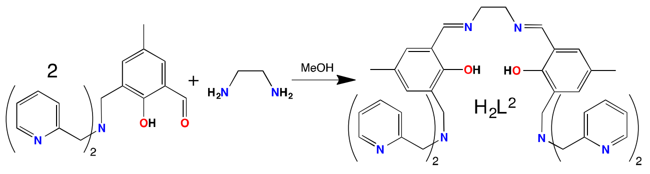
2-formyl-4-methyl-6-(3,5-dimethylpyrazole)phenol (0.244 g, 1.00 mmol) and ethylenediamine (0.03 g, 0.50 mmol) were refluxed together in 30 ml of methanol for 40 minutes (**Scheme 7**). After cooling to room temperature, nickel perchlorate hexahydrate (0.183 g, 0.50 mmol) was added and refluxed for 1 h. $[Cu(2,2'\text{-bpy})(H_2O)_2](NO_3)_2$ (0.3795 g, 1 mmol) was then added and reflux was continued for another 1 h. The yellow solution turned into brownish-green. It was filtered and kept aside. Slow evaporation of methanol gives rod shaped brownish green crystals suitable for X-ray studies. Anal.Calc. For$C_{50}H_{50}Cl_2Cu_2NiN_{12}O_{16}$ (M.W. 1331.71): C, 45.10%; H, 3.78%; N, 12.62%. Found: C, 45.45%; H, 3.58%; N, 12.35%. IR: ν/cm^{-1}: 1081 (ClO_4^-, counter anion), 1643 (C=N), 1383 (μ-NO_3) (**Fig. S6**).



Scheme 7

Synthesis of $[Cu_3(L^2)(NO_3)_2].(ClO_4)_2$ (6)

A mixture of 2-[*N,N-bis*(2-methylpyridyl)aminomethyl]-6-carbaldehyde-4-methylphenol (0.347 g, 1.00 mmol) and ethylenediamine (0.03 g, 0.50 mmol) were refluxed in 30 ml of methanol for 40 minutes (**Scheme 8**). After cooling to room temperature copper perchlorate hexahydrate (0.185 g, 0.50 mmol) was added and refluxed for 1 h. Copper nitrate trihydrate (0.242 g, 1 mmol) was then added and reflux was continued for another 1 h. The yellow solution turned into green. It was filtered and kept aside. Slow evaporation of methanol gives rod shaped green crystals suitable for X-ray studies. Anal.Calc. For$C_{44}H_{44}Cl_2Cu_3N_{10}O_{16}$ (M.W. 1230.44): C, 42.95%; H, 3.60%; N, 11.38%. Found: C, 42.35%; H, 3.98%; N, 11.60%. IR: ν/cm^{-1}: 1079 (ClO_4^-, counter anion), 1604 (C=N), 1385(μ-NO_3) (**Fig. S7**).



Scheme 8

Synthesis of $[Cu_6(L^2)_2Na_2(NO_3)_6(NCS)_4][Cu_3(L^2)(NCS)_2(NO_3)]_2(NO_3)_2.5H_2O$ (7).

2-[*N,N-bis*(2-methylpyridyl)aminomethyl]-6-carbaldehyde-4-methylphenol (0.347g, 1.00 mmol) and ethylenediamine (0.03 g, 0.50 mmol) were refluxed together in 30 ml methanol for 40 minutes. After cooling to room temperature $[Cu(2,2'\text{-bpy})(H_2O)_2](NO_3)_2$ (0.569 g, 1.5 mmol) and sodium thiocyanate (0.098 g, 1.2 mmol) were added and reflux was continued for another 1 h. The yellow solution turned into green. It was filtered and kept aside undisturbed. Slow evaporation of methanol gives rod shaped brownish green crystals suitable for X-ray studies.Anal.Calc. For$C_{214}H_{210}Cu_{12}N_{56}Na_2O_{43}S_8$ (M.W.5305.95): C, 48.31%; H, 3.97%; N, 14.74%. Found: C, 47.70%; H, 3.85%; N, 14.98%.IR: ν/cm^{-1}: 3449 (water, free solvent), 1632 (C=N), 2084 (μ-NCS), 1382 (μ-NO_3) (**Fig. S8**).

Acknowledgements

Financial support from CSIR (Ref.02(2490)/11/EMR -II) and UGC [39-735/2010(SR)] New Delhi, are gratefully acknowledged.R.C., M.R. and I.B. thank the Erasmus Mundus Mobility with Asia program for the Ph.D. fellowship of I. B, the University of Bordeaux, the CNRS, and the Region Aquitaine for financial support.

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†Electronic Supplementary Information (ESI) available: Crystallographic data in CIF format (CCDC no. 972141 (**5**), 972142 (**6**),972143 (**7**), table of bond distances and angles, are deposited in ESI.

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