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Graphical abstract

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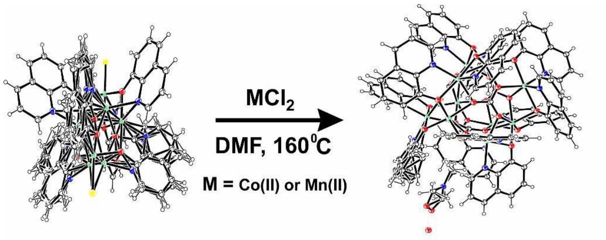

Decanuclear antiferromagnetic metal clusters of Cobalt(II) and Manganese(II)

P. Khakhlary, A. Christopher, A. Mondal, A. K. Powell, J. B. Baruah

Structural and magnetic properties of oxyquinolinate clusters of cobalt(II) and manganese(II) and serendipitous intake of carbonate during synthesis

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Abstract:

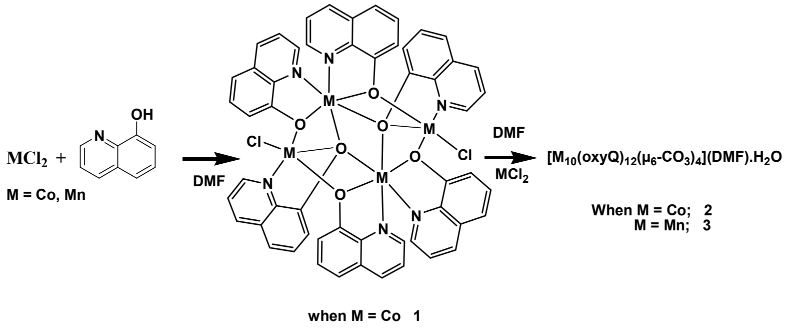
During transformation of a tetra-nuclear cobalt oxiquinolinate cluster to deca-nuclear cobalt oxyquinolinate cluster, serendipitous intake of carbonate ion was observed. By following a similar synthetic path, a deca-nuclear manganese oxyquinolinate cluster was prepared. These clusters show anti-ferromagnetic behavior.

Introduction:

Metal clusters have been attracting attention of structural chemists[1] and are used as precursors of nanomaterials.[2] Some metal clusters are useful magnetic materials[3] and catalysts for organic transformations.[4] There are many low nuclearity clusters of first row transition metals possessing carbonate ligands prepared by intake of carbon dioxide from air.[5] Since carbonate ligand adopts various coordination modes, coordination of carbonate ligand is sensitive to nature of ancillary ligands and oxidation state of metal ions.[6] A metallacycle is more flexible than a cluster, hence a metallacycle under drastic condition should convert to higher nuclear metal cluster/s.[7] In a recent study different nuclearities metallacycles of 1,8-naphthalenedicarboxylate depending on *bis*-chelating ancillary ligands were shown.[8] Main reasons for formation of metallacycles by such a ligand are due to adequate positions and bridging abilities of two carboxylate groups present at 1 and 8-positions of a naphthalene ring. Since, 8-hydroxyquinoline has metal binding sites at 1 and 8 positions of a fused bicyclic ring it is comparable to naphthalene ring and it is also known to form metal clusters.[9] We have taken up synthesis of clusters of 8-oxyquinolinate with cobalt and manganese ions to find out low nuclearity clusters as precursors for synthesis of high nuclearity clusters as novel magnetic properties are expected from clusters depending on metal ions and nuclearities.[3] We have characterized a tetra-nuclear cobalt oxyquinolinate cluster which subsequently converts to deca-nuclear cluster on reaction with additional amount of cobalt ions. A similar synthetic path was extended to synthesize a deca-nuclear manganese oxyquinolinate cluster. Deca-nuclear clusters have carbonate bridging ligands in addition to oxyquinolinate ligands. Structural characterizations and magnetic properties of these clusters are described.

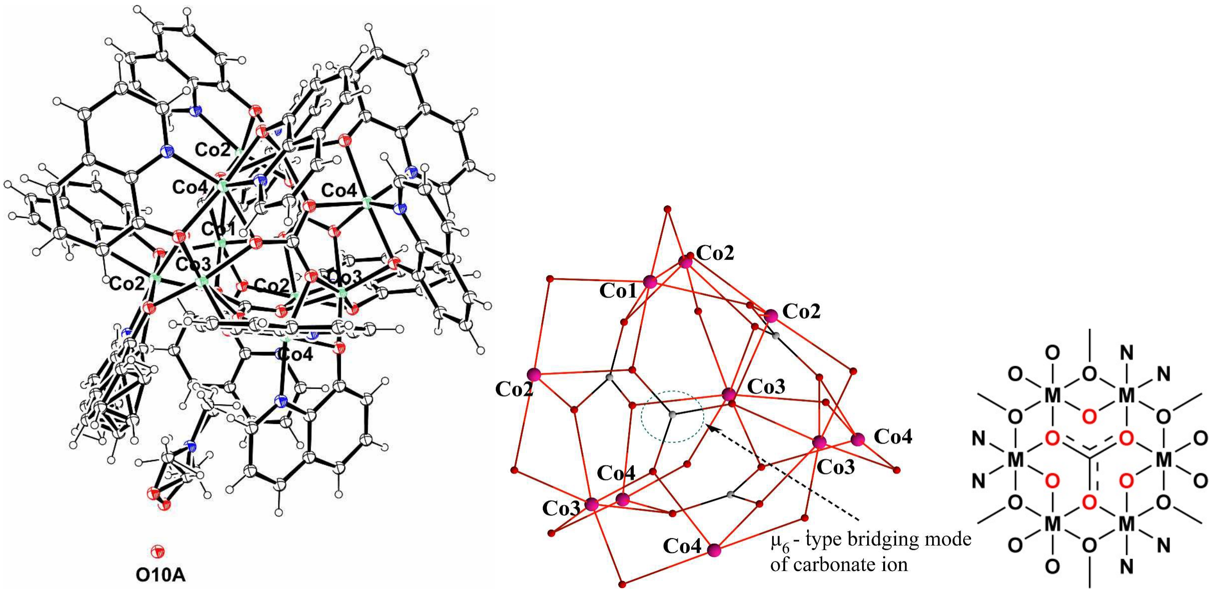
Results and discussion:

Solvothermal reaction of cobalt(II) chloride with 8-hydroxyquinoline (HoxyQ) in 1: 1 ratio resulted a tetra-nuclear cluster with a composition $Co_4(oxyQ)_6Cl_2$. (**1**) (Scheme 1). Tetra-nuclear cobalt cluster was characterized from its elemental analysis and by determining crystal structure. Structure of the cluster is shown in supporting figure 1S and bond connectivity are shown in scheme 1. Structure of the complex has four cobalt ions in two different coordination environments of which two of them have chloride ligands. The cobalt ions have chelated oxyquinoline ligands which also serve as bridging ligands by connecting cobalt ions through μ-oxo-bridges.



Scheme 1: Formation of oxiquinolinate deca-nuclear clusters of Cobalt and Manganese

This cluster reacts further with cobalt(II) chloride under solvothermal condition in dimethylformamide to form a deca-nuclear cluster having a composition $[Co_{10}(oxyQ)_{12}(\mu_6\text{-}CO_3)_4](DMF)\cdot H_2O$ (**2**) which is shown in figure 1(a). Coordination environments showing core of metal ions in the crystal structure of deca-nuclear cobalt cluster is shown in figure 1b. There are examples of formation of copper and nickel carbonate clusters by picking up atomospheric carbondioxide.[12] Metal oxides also under drastic conditions can oxidize dimethylformamide to carbon dioxide.[10] Thus, cluster **2** was formed by reaction of tetra-nuclear cobalt cluster **1** as well as cobalt chloride with carbonate formed *in situ*. Under inert reaction condition or in absence of additional cobalt chloride, deca-nuclear cluster was not formed. Deca-nuclear cluster was also not formed in similar solvothermal reaction carried out in dimethylsulphoxide or in dimethylsulphoxide saturated with carbon dioxide as solvent. A control experiment was carried out by adding sodium carbonate to reaction mixture in dimethylsulphoxide, it did not form cluster **2.** We have also not observed any decomposed product from DMF such as dimethylamine in the reaction mixture when analyzed by GC-MS, thus trace amounts of carbon dioxide from atmosphere under hydrothermal condition could be responsible for formation of cluster **2**; nonetheless, without DMF as solvent the deca-nuclear cluster was not observed. Based on earlier observations[12] and control experiments it is suggested that the intake of carbon dioxide is from atmosphere which is facilitated by dimethylformamide solvent. Carbonate ligands in the cluster are discerned by spectroscopic tools in addition to X-ray structure determination. Presence of carbonate ligands in deca-nuclear cluster **2** was also confirmed chemically, as it liberated carbon dioxide on addition of dilute hydrochloric acid; liberated gas was analyzed by chemical test with lime water. Deca-nuclear cluster **2** contains as many as four carbonate anions each acts as μ^6-bridge[11] to connect six cobalt ions. The presence of solvated molecules of dimethyl formamide is confirmed by recording the thermogravimetry of the cluster. In the thermogram there is a 3.51% weight loss in region of 135°C-164°C (Supporting figure 10S) which is due to loss of solvent of crystallization (theoretical loss= 3.25%).



(a) (b) (c)

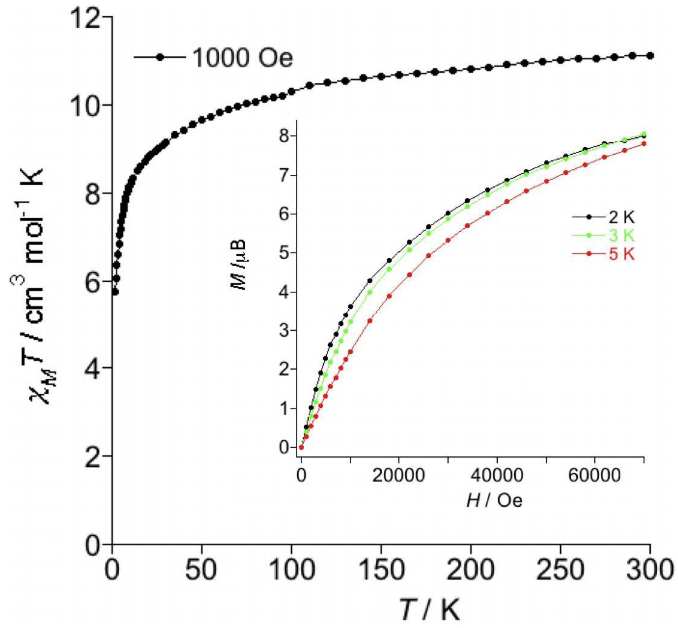
Figure 1: (a) Structure of cluster **2** (drawn with 30% thermal ellipsoids). (b) Core of deca-nuclear cobalt cluster (quinoline rings are not shown for clarity of the structure). (c) Bridging mode of one of the carbonate to hold six metal ions in deca-nuclear metal clusters **2** and **3**.

Binding mode of one of the carbonate ligands in deca-nuclear cluster **2** to knit metal ions within the cluster is shown in figure 1c. Five cobalt(II) ions of the cluster are individually ligated to two oxyquinolinates chelating ligands. These chelating oxyquinolinate ligands are also involved in μ^2-$O_{oxyquinolinate}$ bridge to connect neighboring cobalt ions. This set of cobalt ions of the cluster is anchored to two independent oxygen atoms of two carbonate ligands. Thus, these cobalt ions are in N2O4 type of octa-coordinated environment. On the other hand, there are other five cobalt ions linked to three oxygen atoms of bridging carbonates and three oxygen atoms of bridging oxyquinolinates. This makes an O6 octahedral environment around these cabalt(II) ions. Coordination environments are shown in figure 1c. Observation of two independent environments in deca-nuclear cobalt cluster **2** differs from two different coordination environments for cobalt ions observed in the tetra-nuclear cluster **1**. In cluster **1** oxyquinolinates show chelating as well as bridging mode with cobalt(II) ions. Cluster **1** contains two chloride ligands attached to two cobalt ions. Two cobalt ions are in N2O4 type hexacoordinated distorted octahedral environment whereas other two cobalt ions are in NO3Cl type penta-coordinated environment. Since deca-nuclear cobalt(II) cluster was formed from the reaction of preformed tetra-nuclear cluster, tetra-nuclear cluster can be thought as building block to form deca-nuclear cluster. Accordingly, reacting manganese chloride with HoxyQ in a similar sequence of two step reactions as that of the synthesis of cluster **2**, we synthesized a manganese deca-nuclear cluster $[Mn_{10}(oxyQ)_{12}(\mu_6\text{-}CO_3)_4](DMF)^{\cdot}H_2O$ (**3**). Deca-nuclear manganese cluster **3** is isostructural with deca-nuclear cobalt cluster **2**; thus, structure of **3** is shown in supporting figure 4S. Raman spectra of deca-nuclear cobalt(II) and manganese(II) clusters are similar. Deca-nuclear cobalt cluster **2** shows Raman signals at 1363 cm^{-1} due to antisymmetric stretching, and at 740 cm^{-1} bending mode, whereas deca-nuclear manganese cluster **3** shows these signals at 1361 cm^{-1} and at 737 cm^{-1} respectively. Presence of solvated DMF is confirmed by thermogravimetry of cluster **3** also in which a 3.42% weight loss was observed in the region of 144°C to 190°C due to loss of solvent of crystallization (calculated weight loss for a water molecule and DMF molecule is 3.30%). Support to this observation is obtained from the IR of manganese cluster, it has a C=O stretching signal at 1659 cm^{-1}, on heating at 200°C there is decrease in intensity of this signal (Supporting figure 9S). Cobalt clusters may show both oxidative and reductive couples[13] and reversible couples are associated with cobalt (III) clusters that cause oxidation of organic hydrocarbons.[13b] Clusters **1-3** show ligand based reduction peaks with respect to Ag/AgCl reference electrode at –1.20V (in **1**); -1.23V (in **2**), and -1.18V (in **3**) respectively, and such a reduction peak for free ligand appear at -1.41 V (supporting figures 5S-8S). We have not observed redox peaks originating from redox couples of metal ions in the range of +0.8V to -2V.

Anti-ferromagnetic coupling between metal ions were reflected in temperature dependent magnetic properties of these clusters. For tetra-nuclear cobalt cluster at 1000 Oe, $\chi_M T$ value at

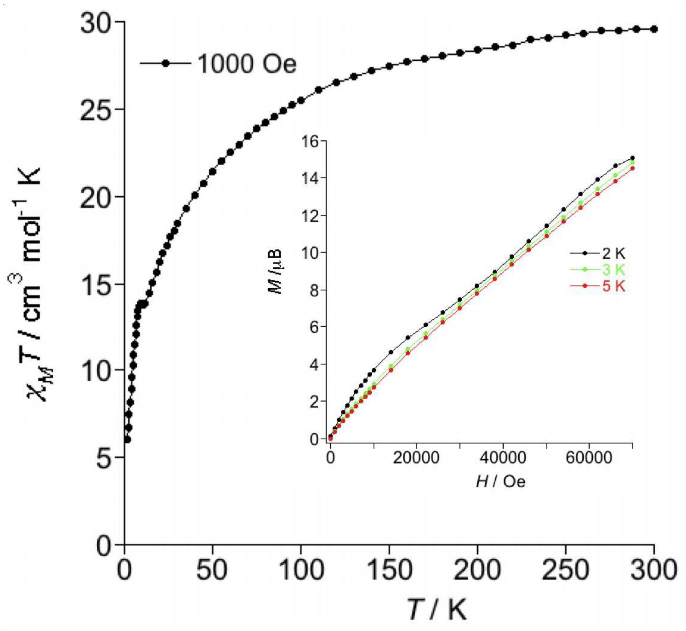
300 K was 11.16 cm^3 mol^{-1} K, which is close to spin only value ($S = 3/2$ and $g_{\mathrm{Co}} = 2.1$; $2.7 < \chi_M T < 3.4$ cm^3 mol^{-1} K per ion) expected for four non interacting high-spin cobalt(II) ions. This behavior is common for cobalt(II) complexes, and can be attributed to orbital contribution of cobalt(II).[14] The $\chi_M T$ values of cluster **1** show a continuous decline to a minimum value of 5.71 cm^3 mol^{-1}K at 2 K (Figure 2a), which is in accordance with anti-ferromagnetic behavior of cobalt (II) ions. *M vs. H* plots of **1** show a saturation value 8.08 μB per formula unit at 2 K and 7 T, which is lower than saturation value of 12 μB for spin-only cobalt(II) ion ($S = 3/2$ and $g_{\mathrm{Co}} = 2.1$). This behaviour also supports an anti-ferromagnetic coupling between cobalt(II) ions in **1** unit.

Magnetic properties investigated by measuring $\chi_M T$ of deca-nuclear cobalt cluster in 2-300 K temperature range at 1000 Oe (where χ_M being the magnetic molar susceptibility per deca-nuclear cobalt unit) is shown in figure 2b. The measured $\chi_M T$ value at 300 K, 29.67 cm^3 mol^{-1} K, lies within expected range for ten high-spin non-interacting cobalt(II) ions: ($S = 3/2$ and $g_{\mathrm{Co}} = 2.1$; $2.7 < \chi_M T < 3.4$ cm^3 mol^{-1} K per ion),[14] with paramagnetic ions exhibiting a significant orbital contribution to their magnetic moment. On lowering temperature, $\chi_M T$ value first smoothly decreases, 9 K, ($\chi_M T = 13.87$ cm^3 mol^{-1} K) and finally decreases more abruptly down to 2.0 K ($\chi_M T = 6.02$ cm^3 mol^{-1} K). Decrease of $\chi_M T$ from room temperature to 13 K is ascribed to effect of spin-orbit coupling (Cobalt(II) ion exhibiting $^4T_{1g}$ ground term) and also to strong anti-ferromagnetic interactions between cobalt(II) ions. *M vs. H* plot of **2** show a value 15.12 μB per formula unit at 2 K and 7 T, which is much lower than saturation value of 30 μB for spin-only cobalt (II) ion ($S = 3/2$ and $g_{\mathrm{Co}} = 2.1$). This behavior also supports strong anti-ferromagnetic coupling between cobalt(II) ions in deca-nuclear cobalt(II) core.



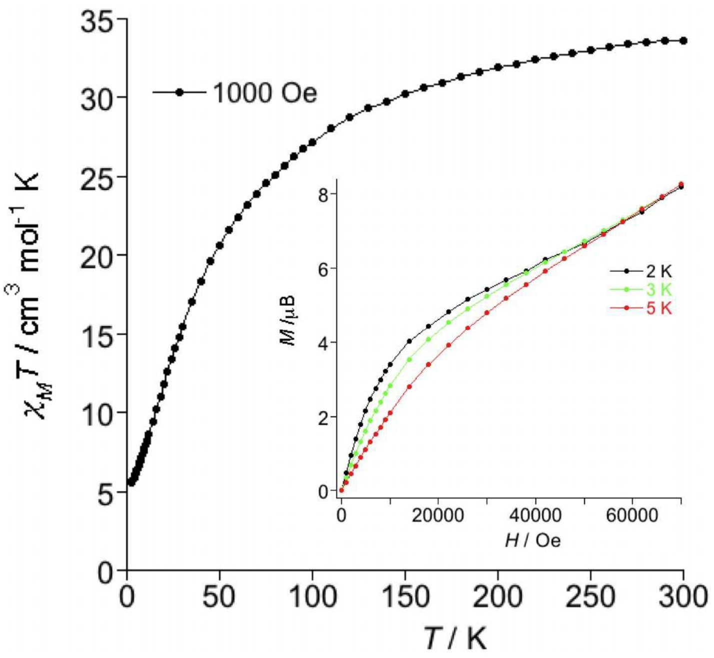
1000 Oe
$\chi_M T$ / cm^3 mol^{-1} K
T / K
0
50
100
150
200
250
300
0
2
4
6
8
10
12
M /μB
H / Oe
2 K
3 K
5 K
0
20000
40000
60000
0
1
2
3
4
5
6
7
8

(a)



1000 Oe
$\chi_M T$ / cm^3 mol^{-1} K
T / K
0
50
100
150
200
250
300
0
5
10
15
20
25
30
M /μB
H / Oe
2 K
3 K
5 K
0
20000
40000
60000
0
2
4
6
8
10
12
14
16

(b)



(c)

Figure 2: Plots of $\chi_M T$ *vs.* T and M *vs.* H (inset) for (a) tetra-nucaler cobalt cluster **1;** (b) deca-nuclear cobalt cluster **2;** (c) deca-nuclear manganese cluster **3**.

The plot of $\chi_M T$ *vs.* T under 1000 Oe external field in temperature range of 300-2 K for deca-nuclear manganese cluster is shown in figure 2c. Room-temperature $\chi_M T$ value for **3** is 33.62 cm^3 mol^{-1} K, which is lower than spin only value of 43.70 cm^3 mol^{-1} K for ten high-spin non-interacting manganese(II) ions (typically the manganese(II) ion has a S = 5/2 state and g_{Mn}= 2.0).[15] As temperature is lowered, the $\chi_M T$ value decrease gradually down to 2 K, where the value have a minimum of 5.51 cm^3 mol^{-1} K at 2 K. This behavior indicates strong anti-ferromagnetic interaction between manganese (II) ions in deca-nuclear manganese unit. M *vs.* H plot of cluster **3** at different temperatures (2 K -5 K) is shown in inset of figure 2c. At 2K, an increase of magnetization was observed with a value of 8.24 μB at 7 T, which is much lower than saturation value 50.0 μB, expected for a spin-only value of ten high-spin non-interacting manganese(II) ions (S = 5/2 and g_{Mn} =2). This behavior also supports strong anti-ferromagnetic coupling between manganese (II) ions in core of deca-nuclear cluster.

In conclusion, deca-nuclear clusters formed by trapping carbonate ions provided avenues to construct new clusters. A tetra-nuclear cobalt(II) cluster is isolated and characterized; it is described as intermediate for formation of deca-nuclear cobalt(II) cluster. These clusters show strong anti-ferromagnetic property, which opens possibilities for synthesis of new magnetic materials with analogous ligands.

Experimental:

All reagents were obtained from Sigma Aldrich (USA) and used as received. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with KBr pallet in the range 4000-400 cm^{-1}. Cyclic-voltammetric experiments were performed on a CHI660A with platinum and glassy carbon electrodes with Ag/AgCl electrode as reference electrode. Cyclic voltammogram were recorded under nitrogen atmosphere of solutions of complexes (10^{-3}M) in DMSO by using tetrabutylammonium perchlorate as supporting electrolyte. X-ray single crystal diffraction data for the clusters were collected on Oxford SuperNova diffractometer. Data refinement and cell reductions were carried out by CrysAlisPro[16a]. Structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software.[16b] All non-hydrogen atoms were refined in the anisotropic approximation against F^2 of all reflections. Crystal parameters of clusters are shown in table 1.

During initial refinement of tetranuclear cobalt cluster, large peaks were found ca. 1Åfrom the Co atoms, which were large enough to refine as O atoms with realistic temperature factors, but which were both chemically and structurally unrealistic. It was noted that when these "ghost peaks" and the Co atoms were taken together they formed regular hexagons or equilateral triangles perpendicular to the Cl···Cl axis, and that this axis was coincident to the sixfold or threefold axes of these hexagons and triangles. Furthermore, the eight ghost peaks could be arranged into two sets of four, each of which had peak-peak distances very similar to the Co-Co distances. Given also the almost exact trigonal symmetry of the external shape of the molecule, the presence of threefold whole-molecule disorder was clear.

Assignment of the cobalt atoms and "ghost peaks" all as partial-occupancy cobalt atoms, with the total occupancy of each set of three cobalt restrained to unity and a common temperature factor assigned to each set of three cobalt atoms, showed relative occupancies of ca. 64:19:17. The temperature factors of the cobalt atoms were then restrained to be similar, rather than constrained to be equal. Refinement of the organic ligands using isotropic atoms of occupancy

0.64, with the quinoline ring systems each constrained to two fused regular hexagons (AFIX 116) allowed most of the atoms of the minor components of the ligands to be located. Refinement of these, again using AFIX 116, with similarity restraints to all C-O distances and the oxygens restrained to lie in the plane of their respective quinoline rings, was relatively straightforward. The C, N and O atoms of the major ligand components could then be refined ansiotropically, with similarity restraints (SIMU) applied to the thermal parameters of partial atoms closer than 0.4 Å to each other. In the final refinement, the relative occupancies were fixed to values adding up to exactly unity, and the structure refined to convergence.

Disorders in cobalt and manganese decanuclear clusters were also observed. One of the ligands in the asymmetric unit showed twofold disorder by "flapping" about the O6-N2-C20 axis. It was modelled with isotropic C atoms of 50% occupancy. The phenolic rings of the part ligands were constrained to rigid hexagons, while geometrical similarity restraints were applied to the remaining C-N and C-C bonds. The lattice DMF molecule also showed 50:50 disorder, and geometric restraints were applied. The hydrogen atoms of lattice water (half of a water per cluster) could not be modelled in the structure of decanuclear clusters. Half of an H_2O corresponds to 1 H atom.

Synthesis of tetra-nuclear cobalt cluster **1**: A mixture of 8-hydroxyquinoline (0. 31 g, 2 mmol), $CoCl_2.6H_2O$ (0.28 g, 2 mmol) and dimethylformamide (10 mL) was stirred for 15 minutes. The resulting solution was transferred to a Teflon-lined autoclave and kept under autogenous pressure at 160 °C for 2 days. After slow cooling to room temperature, pink block crystals of tetra-nuclear cobalt cluster were obtained. Isolated yield based on cobalt 45%. Elemental anal calcd for $C_{54}H_{36}Cl_2N_6O_6Co_4$, C: 55.36%, N: 6.05%, H: 3. 10%; found, C: 55. 31 %, N: 7.62 %, H: 3.16 %. IR(KBr, cm^{-1}): 3048 (w), 1658 (w), 1603 (w), 1577 (s), 1499 (s), 1465 (s), 1424 (s), 1379 (s), 1316 (s), 1269 (s), 1233 (w), 1177 (w), 1107 (s), 1032 (w), 908 (w), 826 (m), 789 (m), 756 (m), 733 (m), 645 (w), 600 (w), 507 (w).

Synthesis of deca-nuclear cobalt cluster **2**: A mixture of $Co_4(oxyQ)_6Cl_2$ (0.40 g, 3 mmol), $CoCl_2.6H_2O$ (0.23 g, 1 mmol) and dimethylformamide (10 mL) was stirred for 15 minutes. The resulting solution was then transferred to a Teflon-lined autoclave and kept under autogenous pressure at 160°C for 2 days. After slow cooling of the solution to room temperature, pink block crystals of deca-nuclear cobalt cluster were obtained in 72% yield. Elemental anal. Calcd. for $C_{121}H_{95}N_{15}O_{28}Co_{10}$; C: 51.97%, N: 7.51%, H: 3.42%; found, C: 51.68%, N: 7.77%, H: 3.31%. IR(KBr, cm^{-1}): 3042 (w), 2925 (w), 1659 (s), 1602 (w), 1574 (s), 1492 (s), 1460 (s), 1379 (s), 1321 (s), 1278 (m), 1227 (w) 1108 (s), 1027 (w), 906 (w), 824 (m), 788 (m), 745 (m), 648 (w), 602 (w), 570 (w), 499 (w). Raman (KBr, cm^{-1}): 3064 (w), 1580 (s), 1363 (s), 740 (w).

Synthesis of deca-nuclear manganese cluster **3**: A yellowish precipitate (0.40 g) obtained from a reaction $MnCl_2.4H_2O$ (0.20 g, 1 mmol) with 8-hydroxyquinoline (0.16g, 1 mmol), analogously to the synthesis of tetra-nuclear cobalt complex **1,** which was taken with $MnCl_2.4H_2O$ (0.20 g, 1 mmol) in dimethylformamide (10 mL) and was stirred for 15 minutes. The solution thus prepared was transferred to a Teflon-lined autoclave and kept under autogenous pressure at 160 °C for 2 days. After slow cooling to room temperature yielded pink block crystals of deca-nuclear manganese cluster **3** in 68% yield. Elemental anal. Calcd. for $C_{121}H_{95}N_{15}O_{28}Mn_{10}$; C: 52.72%, N: 7.67%, H: 3.47%; found, C: 52.11%, N: 8.48%, H: 3.52 %. IR (KBr, cm^{-1}): 3419 (w), 3041 (w), 2924 (w), 1660 (m), 1601 (w), 1572 (m), 1487 (s), 1452 (s), 1383 (s), 1321 (s), 1278 (m), 1230 (w), 1172 (w), 1107 (s), 1058 (w), 1029 (w), 904 (w), 824 (m), 789 (m), 748 (m), 731 (m), 646 (w), 601 (w), 567 (w), 492 (w). Raman (KBr, cm^{-1}): 3054 (w), 1572(s), 1361(s), 870 (s).

Table 1: Crystallographic parameters of clusters **1-3**

Compound No.	**1**	**2**	**3**
Formulae	$C_{54}H_{36}Cl_2N_6O_6\ Co_4$	$C_{121}H_{93}N_{15}O_{27.5}Co_{10}$	$C_{121}H_{93}N_{15}O_{27.5}Mn_{10}$
Mol. wt.	1171.51	2787.41	2747.51
CCDC No	1025061	1022853	1022854
Crystal system	Monoclinic	Cubic	Cubic
Space group	$P2_1/n$	*Pa-3*	*Pa-3*
Temperature (K)	296 (2)	296 (2)	296 (2)
Wavelength (Å)	0.71073	0.71073	0.71073
a (Å)	11.0742(4)	28.1201(4)	28.2948(3)
b (Å)	13.6865(5)	28.1201(4)	28.2948(3)
c (Å)	17.0032(7)	28.1201(4)	28.2948(3)
α (°)	90	90	90
β (°)	105.997(3)	90	90
γ (°)	90	90	90
V ($Å^3$)	2477.33(16)	22235.7(6)	22652.7(7)
Z	2	8	8
Density/gcm^{-3}	1.572	1.665	1.611
Abs. Coeff. /mm^{-1}	1.482	1.538	1.160
Abs. correction	multi-scan	multi-scan	multi-scan
F(000)	1184	11320	11160
Total no. of reflections	4992	7035	7709
Reflections, $I > 2\sigma(I)$	3194	4024	3366

Max. 2θ (°)	52.74	51.31	52.72
Ranges (h, k, l)	$-13 \leq h \leq 13$ $-17 \leq k \leq 17$ $-21 \leq l \leq 21$	$-34 \leq h \leq 34$ $-34 \leq k \leq 36$ $-34 \leq l \leq 34$	$-35 \leq h \leq 35$ $-35 \leq k \leq 35$ $-35 \leq l \leq 35$
Completeness to 2θ (%)	0.986	0.998	0.998
Data/ Restraints / Parameters	4992/384/409	7035/62 /486	7709/59/486
Goof (F^2)	1.048	1.067	1.025
R indices [$I > 2\sigma(I)$]	0.0521	0.0679	0.0844
R indices (all data)	0.0942	0.1348	0.1927

Supporting information: CIF files are deposited to Cambridge Crystallographic Database and they have CCDC numbers 1022853, 1022854, 1025061. Cyclic voltamograms and thermograms of the clusters, ORTEP diagram of structure of clusters **1** and **3**, tables for metal-ligand bond parameters are available.

References:

1. (a) M. Calhorda, D. Braga, F. Grepioni, *Metal clusters - The relationship between molecular and crystal structure,* 1999, Wiley-VCH, New York. (b) P. Braunstein, L. A. Oro, P. R. Raithby, eds. *Metal Clusters in Chemistry*; 1999, Wiley-VCH, Weinheim. (c) K. H. He, Y. W. Li, Y. Q. Chen, W. C. Song, X. H. Bu, *Cryst. Growth Des.*, 2012, **12**, 2730-2735. (d) X. Zhao, B. Xiao, A. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *Science,* 2004, **306**, 1012. (e) Y, Cui, Y. Yue G. D. Qian, B. L. Chen, *Chem. Rev.,* 2012, **112**, 1126-1162. (f) A. Karmakar, J. B. Baruah, *Polyhedron,* 2008, **27**, 3409-3416. (g) G. Aromi, S. M. J. Aubin, M. A. Bolcar, G. Christou, H. J. Eppley, K. Floting, D. N. Hedrickson, J. C. Huffman, R. C. Squire, H. -L. Tsai, S. Wang, M. W. Wemple, *Polyhedron*, 1998, **17**, 3005-3020.

2. (a) G. Schmid, D. Fenske, *Phil. Trans. Royal Soc. A,* 2010, **368**, 1207-1210 (b) M. T. Reetz, W. Helbig, *J. Am. Chem. Soc.*, 1994, **116**, 7401-7402. (c) B. Corain, M. Zecca, P. Canton, P. Centomo, *Phil. Trans. Royal Soc. A,* 2010, **368**, 1495-1507.

3. (a) R. Sessoli, H. -L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.*, 1993, **115**, 1804-1816. (b) R. C. Squire, S. M. J. Aubin, K. Folting, W. E. Streib, G. Christou, D. N. Hendrickson*, Inorg. Chem.*, 1995, **34**, 6463-6471. (c) A. Andriotis, N. Lathiotakis, M. Menon, *Chem. Phys. Letters,* 1996, **260**, 15-20. (d) G. Christou, D. Gattesci, D. N. Hendrickson, R. Sessoli, *MRS Bulletin*, 2000, 66-71.

4. (a) G. Suss-Fink, M. Jahncke, *Synthesis of organic compounds catalyzed by transition metal clusters*. 1998, Wiley-VCH, New York. (b) A. Smith, J. Basset, *J. Molecular Catal.,* 1977, **2**, 229-241. (c) M. Ichikawa, L. Rao, T. Kimura, A. Fukuoka, *J. Molecular Catal.,* 1990, **62**, 15-35.

5. (a) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. -H. Bae, J. R. Long. *Chem. Rev.,* 2012, **112**, 724-781. (b) D. Armentano, N. Marino, T. F. Mastropietro, J. Martinez-lillo, J. Cano, M. Julve, F. Lloret, G. DeMunno, *Inorg. Chem.,* 2008, **47**, 10229-10231.

6. (a) A. Escuer, R. Vicente, S. B. Kumar, X. Solans, M. Font-Bardia, *J. Chem. Soc., Dalton Trans.,* 1997, 403-407. (b) A. Escuer, R. Vicente, S. B. Kumar, X. Solans, M. Font-Bardia, *J. Chem. Soc. Dalton Trans*., 1998, 3473-3477

7. C. Artner, M. Czakler, U. Schubert, *Chem. Eur. J.,* 2014, **20**, 493-498.

8. J. K. Nath, Y. Lan, A. K Powell, J. B. Baruah, *Zeitschrift für Anorg. Allgem. Chemie,* 2013, **639**, 2250-2257.

9. J. Wang, Q. Wang, Y. Sun, Y. Wang, G. Zhao, Y. Cui, *J. Serb. Chem. Soc.,* 2011, **76***,* 529-537. (b) P. Khakhlary, J. B. Baruah, *J. Chem. Sci., in press* (2014).

10. N. Grosjeean, C. Descorme, M. Besson, *Appl. Catal. B-Environ,* 2010, 97B, 276-283.

11. (a) A. Escuer, R. Vicente, S. B. Kumar, F. A. Mautner, *J. Chem. Soc. Dalton Trans.,* 1998, 3473-3479. (b) M. -L. Tong, M. Monfort, J. Modesto, C. Juan, X. -M. Chen, X. -H. Bu, M. Ohba, S. Kitagawa. *Chem. Commun*., 2005, 233-235. (c) D. Armentano, N. Marino, T. F. Mastropietro, J. Martınez-Lillo, J. Cano, M. Julve, F. Lloret, G. D. Munno, *Inorg. Chem.*, 2008, **47**, 10229-10231.

12. (a) A. Graham, S. Meier, S. Parsons, R. E. P. Winpenny, *Chem. Commun.*, 2000, 811-812. (b) T. Tanase, S. Nitta, S. Yoshikawa, K. Kobayashi, T. Sakurai, S. Yano, *Inorg. Chem.*, 1992, **31**, 1058.

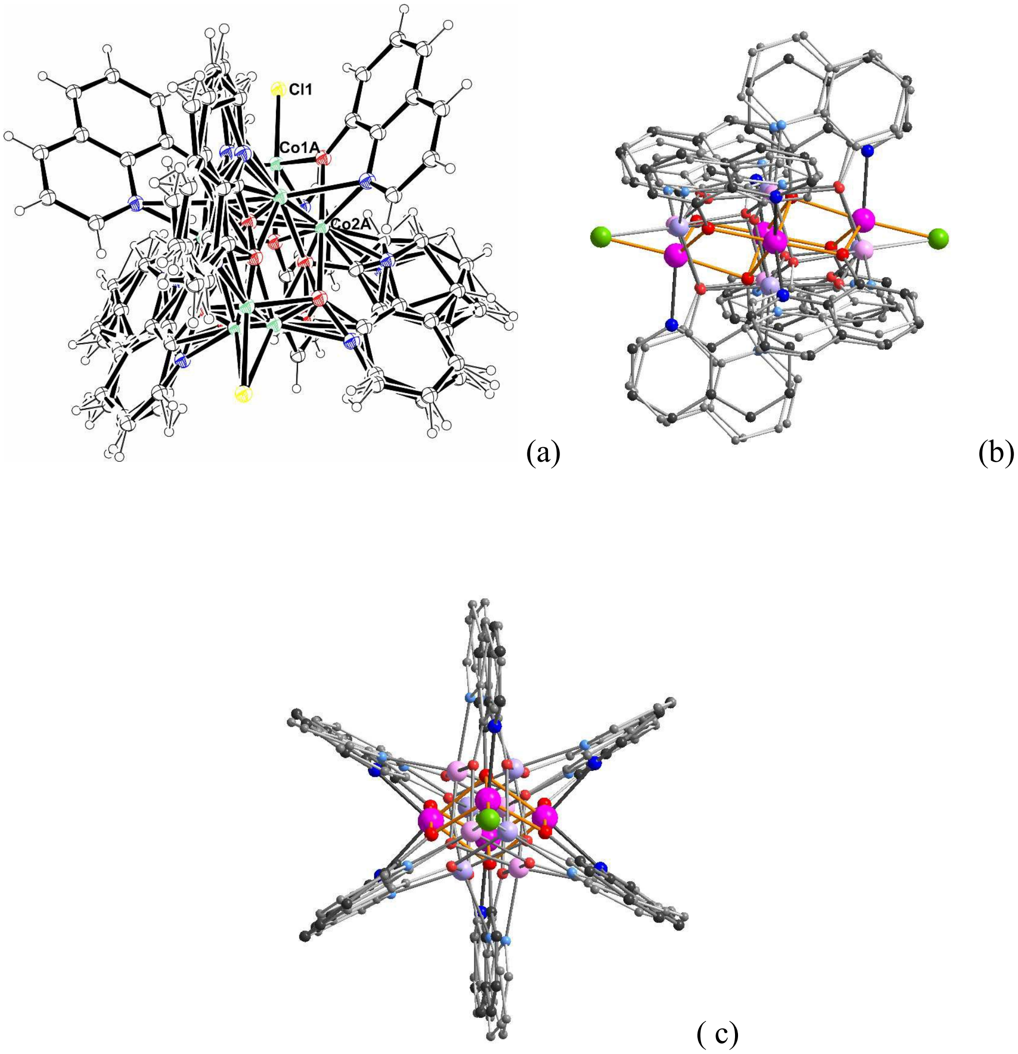
13. (a) Q. -P. Huang, G. Li, Gui, S. -H. Huang, S. -H. Zhang, H. -Y. Zhang, *Chinese J. Struct. Chem.,* 2014, **33**, 1135-1140. (b) R. Chakrabarty, S. J. Bora, B. K. Das, *Inorg. Chem.,* 2007, **46**, 9450-9462. (c) L. Lisnard, P. Mialane, A. Dolbecq, J. Marrot, J. M. Clemente-Juan, E. Coronado, B. Keita, P. deOliveira, L. Nadjo, F. Secheresse, *Chem. Eur. J.,* 2007, **13**, 3525-3536. (d) R. L. Bedard, L. F. Dahl, *J. Am. Chem. Soc.*, 1986, **108**, 5933-5942.

14. F. Lloret, M. Julve, J. Cano, R. Ruiz-Garcia, E. Pardo, *Inorg. Chim. Acta*, 2008, **361,** 3432-3445.

15. (a) D. F. Li, S. Parkin, G. B. Wang, G. T. Yee, A. V. Prosvirin, S. M. Holmes, *Inorg. Chem*., 2005, **44,** 4903-4905. (b) E. Pardo, M. Verdaguer, P. Herson, H. Rousseliere, J. Cano, M. Julve, F. Lloret, R. Lescouezec, *Inorg. Chem.* 2011, **50,** 6250-6262.

16. (a) CrysAlisPro Oxford Diffraction Ltd. version 1, 2009, 171. 33.34d. (b) G. M. Sheldrick *Acta Crystallogr.,* 2008, **A64**, 112-122.

Supporting information:



(a)

(b)

(c)

Figure 1S: (a)Structure of tetra-nuclear cobalt cluster **1**; (ORTEP drawn with 30 % thermal ellipsoids, cobalt 1 is disordered and shared between three sites). (b) and (c) are views from two directions of the cluster to show disorder.

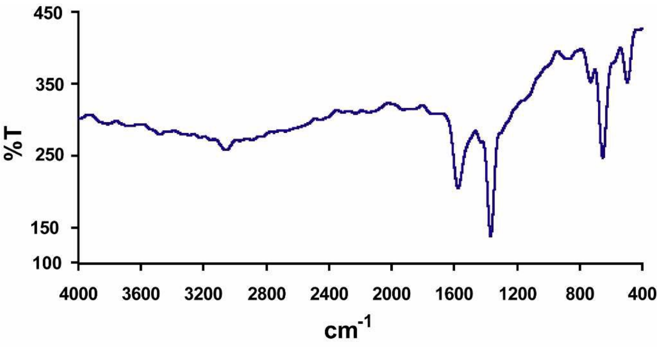


Figure 2S: Raman spectra of deca-nuclear cobalt cluster **2**.

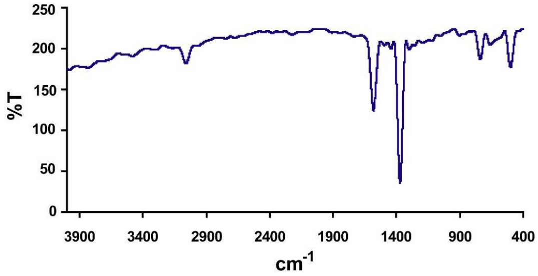


Figure 3S: Raman spectra of deca-nuclear manganese cluster **3**.

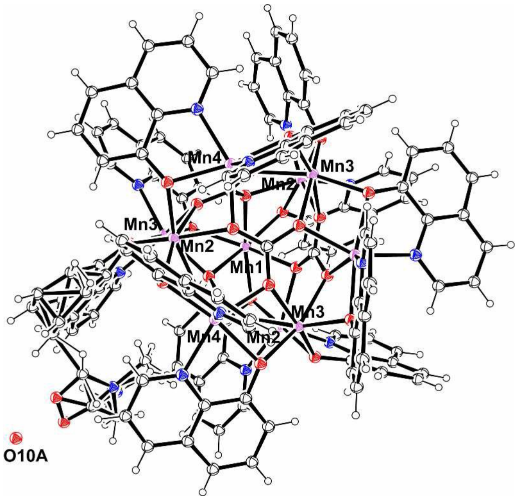


Figure 4S: Deca-nuclear core of manganese cluster **3** (drawn with 30% thermal ellipsoids).

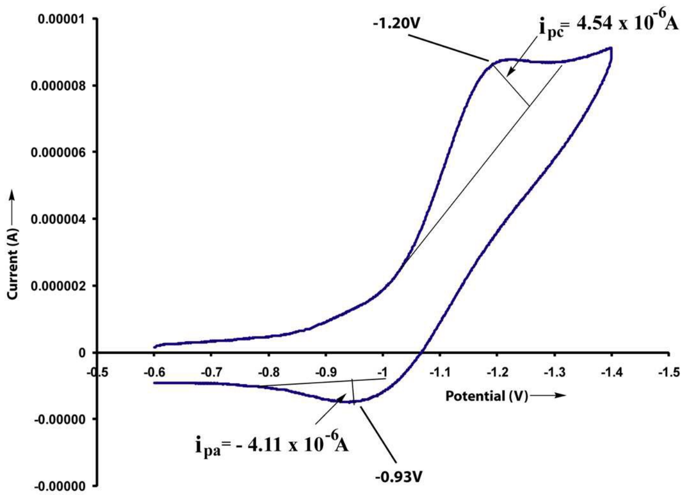


Figure 5S: Cyclic voltamogram of tetra-nuclear cobalt cluster **1** (+ ve scan, sweep rate 100mV/sec, Ag/AgCl as reference electrode, 10^{-3}M in DMSO, TBAP as supporting electrolyte).

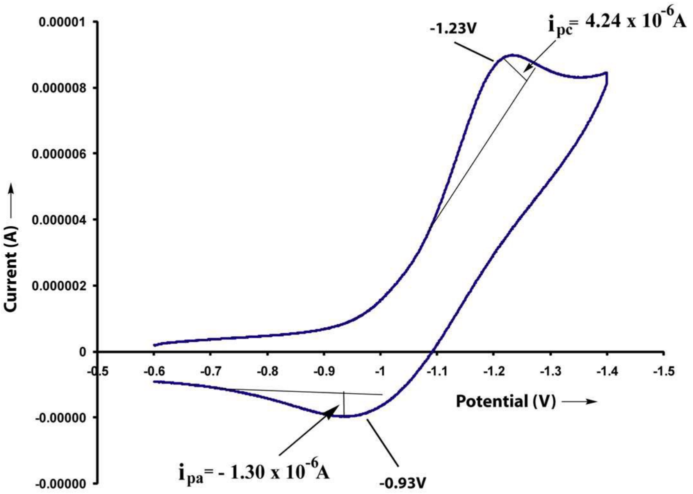


Figure 6S: Cyclic voltamogram of deca-nuclear cobalt cluster **2** (+ve scan, sweep rate 100 mV/sec, Ag/AgCl as reference electrode, 10^{-3}M in DMSO, TBAP as supporting electrolyte).

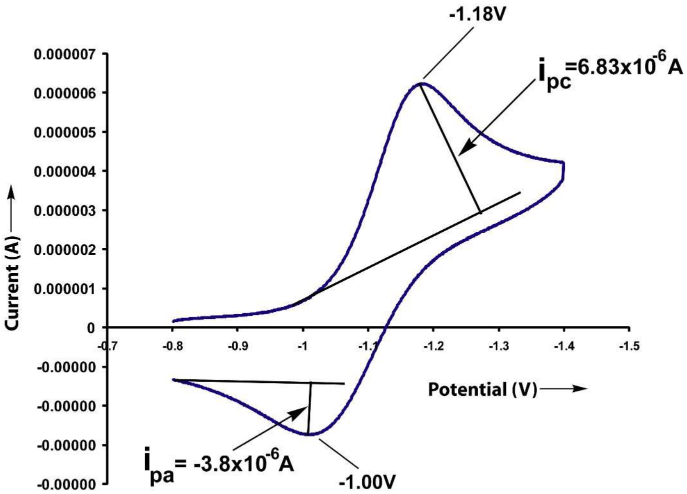


Figure 7S: Cyclic voltamogram of deca-nuclear manganese cluster **3** (+ve scan, sweep rate 100mV/sec, Ag/AgCl as reference electrode, 10^{-3}M in DMSO, TBAP as supporting electrolyte).

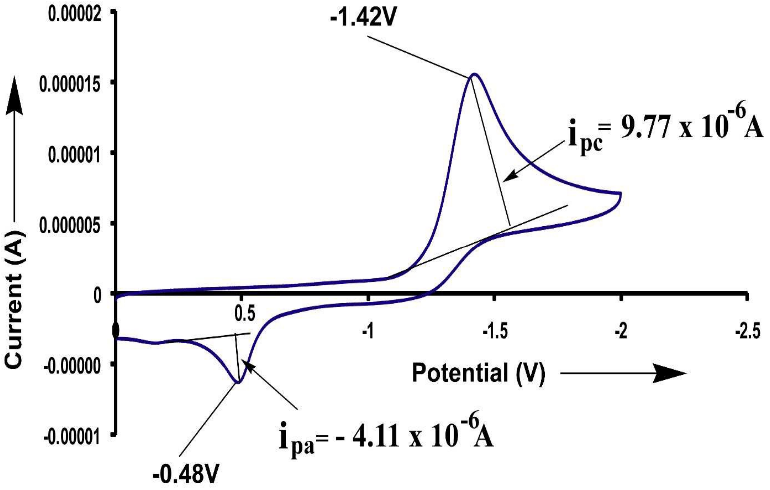


Figure 8S: Cyclic voltamogram of 8-hydroxyquinoline (+ ve scan, sweep rate 100mV/sec, Ag/AgCl as reference electrode, 10^{-3}M in DMSO, TBAP as supporting electrolyte)

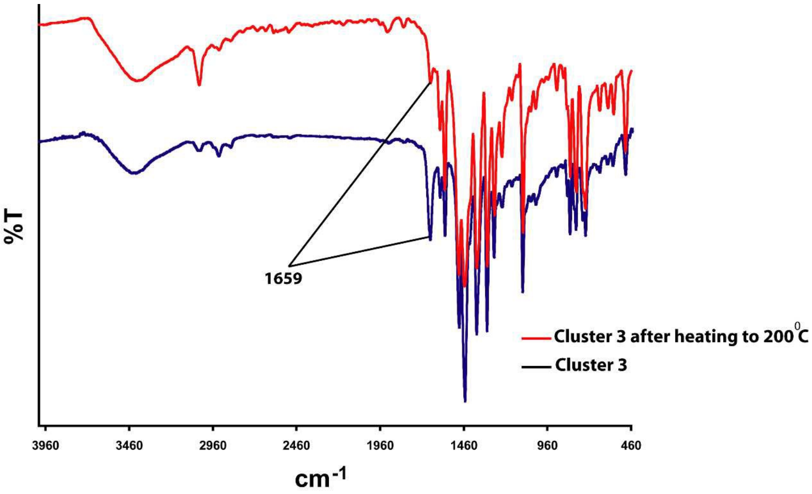


Figure 9S: FT-IR spectra (KBr) of cluster **3** (blue) and after heating cluster **3** at a temperature of 200°C.

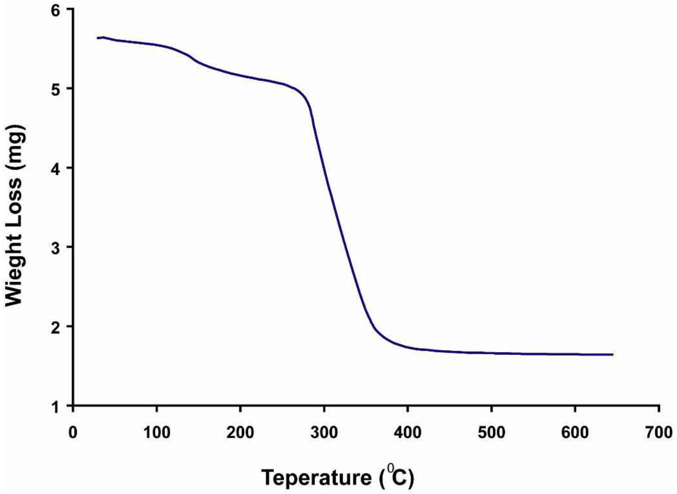


Figure 10S: Thermogravimetry of cluster **2** showing weight loss in the temperature range 135°C to 164 °C due to loss of water and DMF (Experimental loss = 3.51%, theoretical loss = 3.25%)

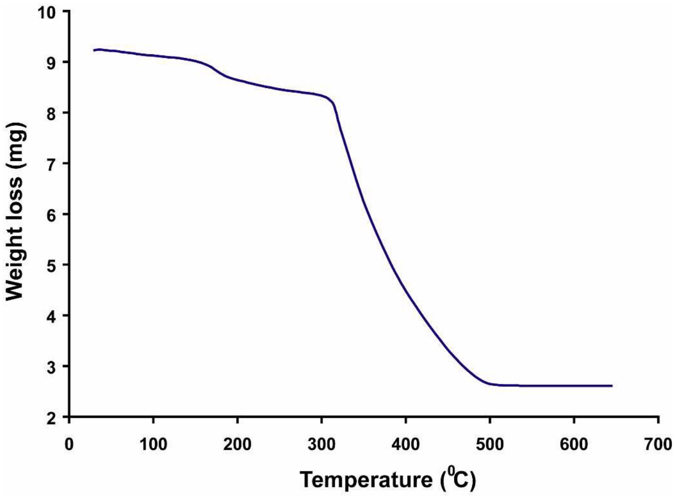


Figure 11S: Thermogravimetry of cluster **3** showing weight loss in the temperature range 144°C to 190 °C due to loss of water and DMF (Experimental loss = 3.42%, theoretical loss = 3.30%)

Table 1S: Some metal ligand bond parameters in clusters **2** and **3**

Bond lengths	Bond (Å)	Bond (Å)	Bond angles	Angle (°)	Angle (°)	Bond angles	Angle (°)	Angle (°)
	Cluster 2	Cluster 3		Cluster 2	Cluster 3		Cluster 2	Cluster 3
M1-O1	2.068(4)	2.127(5)	O1-M1-O2	77.67(16)	78.82(19)	O6-M4-N3	152.6(2)	150.6(3)
M1-O2	2.166(4)	2.245(5)	M1-O2-M2	94.04(17)	92.80(19)	O1-M2-N2	97.71(19)	97.4(2)
M2-O1	2.088(4)	2.146(5)	O1-M2-O2	78.30(16)	80.00(19)	O5-M4-O7	104.77(17)	105.9(2)
M2-O2	2.119(4)	2.175(5)	O3-M3-O6	89.91(16)	87.22(19)	O2-M2-O4	101.74(17)	103.3(2)
M2-O4	2.099(5)	2.146(6)	O1-M2-O4	176.98(17)	173.4(2)	O5-M4-O6	83.90(17)	84.19(19)
M3-O6	2.142(4)	2.218(5)	O3-M3-O8	168.68(17)	166.0(2)	O2-M2-N1	155.6(2)	154.7(3)
M3-O7	2.055(4)	2.111(5)	O1-M2-N1	79.12(19)	76.6(3)	O2-M2-N2	99.05(19)	98.2(2)
Mn4-N3	2.091(6)	2.173(9)						

Table 2S: Some metal ligand bond parameters of cluster **1**.

Bond lengths	Bond (Å) Cluster 1	Bond angles	Angle (°) Cluster 1
Co1A-Cl1	2.329(4)	Cl1-Co1A- O1A	105.6(3)
Co2A-O1A	2.065(11)	Cl1-Co1A- O2A	175.8(3)
Co2A-O2A	2.092(16)	Cl1-Co1A- O3A	106.0(4)
Co2A-N1A	2.079(14)	O1A-Co2A- O2A	78.8(4)
Co1A-N2A	2.086(11)	O1A-Co2A -N1A	79.5(5)