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# Construction of Two Discrete Molecular High-Nuclearity Copper(II) Complexes as Heterogeneous Catalysts for Oxidative Coupling Polymerisation of 2,6-Dimethylphenol

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Reaction of a rigid conjugated clamp-like multi-pyridine ligand *N*,*N*′-bis(pyridin-3-yl)-2,6-pyridinedicarboxamide ($H_2L$) with $CuSO_4·5H_2O$ or $Cu(OAc)_2$ resulted in the formation of two high-nuclearity, discrete molecular copper(II) complexes, namely $[Cu_{10}(H_2L)_5(SO_4)_8(\mu_3\text{-}OH)_4(H_2O)_2]·4CH_3CH_2OH·7H_2O$ (**1**) and $[Cu_6(L)_4(CH_3COO)_4]·2DMF·6H_2O$ (**2**). In **1**, ten copper atoms are engaged by five $H_2L$ ligands, eight $SO_4^{2-}$ and four $\mu_3$-OH groups to form a novel decanuclear copper complex which sits on a crystallographic twofold axis passing through the centre of the complex. The structure of **2** features a hexanuclear copper cage and a crystallographic centre of inversion is at the mid-point of the compound. The rigid conjugated clamp-like $H_2L$ ligands, polydentate in nature, form a "coordination pocket" arising from their "arms" to entrap the copper atoms and play an important role in the assembly of discrete molecular high-nuclearity complexes **1** and **2**. Applications of **1** and **2** as heterogeneous catalysts for the oxidative polymerisation of 2,6-dimethylphenol showed very promising results at ambient temperature and these novel catalytic systems are very mild, efficient, regioselective and easily recyclable. The interesting catalytic properties of **1** and **2** can be attributed to their particular structural characteristics and their unusual reactivities based on cooperativity or electron transfer between multicopper centres. Magnetic studies of these copper(II) cages indicate antiferromagnetic behaviour.

## Introduction

High-nuclearity, discrete molecular copper(II) compounds have attracted a substantial amount of research interest due to their possible utility in modelling the multimetal active sites of metalloproteins,[1] in molecular magnets,[2] with a special emphasis on single-molecule magnets (SMM) and for devising nanometre-sized materials for potential use in nanoscience.[3] Unfortunately, though some high-nuclearity, discrete molecular copper(II) compounds have been reported in the literature,[2,4] there are few reports on their applications as catalysts.[5] In particular, their utility as heterogeneous catalysts has rarely been reported to date.[6] However, we think that catalysis should have been one of the most promising applications of such materials not only because they are generally thermally stable but also because the assembly of a large number of $Cu^{II}$ ions having a $d^9$ electronic configuration in a single molecule generates unusual reactivities based on cooperativity or electron transfer between metal centres.[5] In addition, they are readily tuneable and, as a result, heterogenised size- and shape-selective catalysts can be achieved by a judicious choice of bridging ligands. Hence, intensive studies on high-nuclearity copper compounds should be undertaken instantly to develop new complexes with useful catalytic performance and to elucidate the relationship between structure and reactivity of the natural active sites.

How then can we find a simple synthetic method to generate discrete molecular high-nuclearity copper(II) complexes with *N*,*O*-polydentate ligands ? In most cases, among the factors that induce the self-assembly processes, the ligand plays a crucial role in deciding between polynuclear vs. extended structures of the metal complexes. One of the popular strategies of fabricating discrete molecular high-nuclearity structures is to design ligands which have the ability to bind the metal centres together within a limited area by utilising their coordination sites. In addition, the anions, such as $SO_4^{2-}$ and $OAc^-$, also play a very important role in the assembly of discrete molecular high-nuclearity structures because of their bridging effect. Our approach used here is to utilise a rigid conjugated clamp-like multi-pyridine ligand, *N*,*N*′-bis(pyridin-3-yl)-2,6-pyridinedicarboxamide ($H_2L$), which is polydentate in nature and can form a "coordination pocket" arising from its "arms" to entrap the coordinated metal centres.

In addition, the copper(II)-catalysed oxidative coupling of 2,6-dimethylphenol (DMP) constitutes a broad and interesting research topic both from a biological and a synthetic point of view.[7] This oxidative reaction provides a

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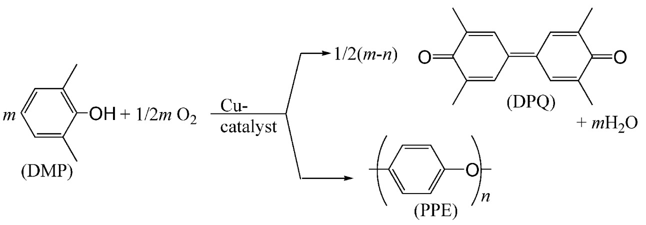
convenient and industrial method of preparing poly(phenylene ether) (PPE), a valuable amorphous high-performance thermoplastic in engineering. Moreover, this polymerisation proceeds at room temperature and is an ideal atom-economical reaction that does not require any leaving groups (Scheme 1).[7b] Since this reaction was first found by Hay et al. in 1959,[8] many homogeneous catalytic systems including heteropolyacids, Schiff base complexes of $Co^{II}$, $Mn^{II}$, $Fe^{II}$, $Ni^{II}$ and $Cu^{II}$ as well as transition metal salts of Fe, Cu, Ru, Mo, etc., have been extensively employed to accomplish this transformation.[7] Recently, considerable effort has been made by our group concerning the correlations between the structural and chemical factors of some $Cu^{II}$-containing complexes with the activities and selectivities of the oxidative reaction.[9] Although it has been generally observed that some $Cu^{II}$-containing complexes based on *N*-heterocyclic ligands with coordinatively unsaturated metal sites showed very promising results for the reaction because they can afford competent size- or shape-selective homogeneous or heterogeneous catalysts for the reaction, the systematic structure-reactivity relationship still remains elusive. Furthermore, to the best of our knowledge, there are few heterogeneous catalysts for this reaction[7b] and the use of high-nuclearity copper(II) complexes still remains an unexplored area of research.



Scheme 1. Overall reaction scheme for the oxidative coupling of DMP to PPE and DPQ.

Herein, through direct reaction of the $H_2L$ ligand with $CuSO_4{\cdot}5H_2O$ or $Cu(OAc)_2$, we acquired two novel discrete molecular high-nuclearity copper(II) complexes, namely $[Cu_{10}(H_2L)_5(SO_4)_8(\mu_3\text{-}OH)_4(H_2O)_2]{\cdot}4CH_3CH_2OH{\cdot}7H_2O$ (**1**) and $[Cu_6(L)_4(CH_3COO)_4]{\cdot}2DMF{\cdot}6H_2O$ (**2**). Preliminary application of these polynuclear $Cu^{II}$ complexes as heterogeneous catalysts showed very promising results for the oxidative polymerisation of DMP at ambient temperature and as novel catalytic systems they are very mild, efficient, regioselective and easily recyclable. Furthermore, the magnetic properties of **1** and **2** have been investigated.

## Results and Discussion

### Structure of $[Cu_{10}(H_2L)_5(SO_4)_8(\mu_3\text{-}OH)_4(H_2O)_2]{\cdot}4CH_3CH_2OH{\cdot}7H_2O$ (1)

X-ray diffraction reveals that **1** belongs to the monoclinic space group *C2/c*. In **1**, ten copper atoms are engaged by five $H_2L$ ligands, eight $SO_4^{2-}$ and four $\mu_3$-OH groups to form a novel decanuclear copper complex which sits on a crystallographic twofold axis passing through Cu2 and Cu6 (Figure 1 top). Six crystallographically independent copper atoms are present (Figure 1 bottom). Cu1, Cu3, Cu4, and Cu5 reside in distorted trigonal bipyramidal coordination environments with the N atoms from the $H_2L$ ligands and the O atoms from the $H_2O$, $SO_4^{2-}$ or $\mu_3$-OH groups. Cu2 is six-coordinate by binding four O atoms (O7, O7A, O18, and O18A) from four $SO_4^{2-}$ groups (with Cu–O = 2.17 Å) and two O atoms (O23 and O23A) from two $\mu_3$-OH groups (with Cu–O = 2.00 Å). This gives a tetragonally elongated octahedral environment derived from the Jahn–Teller effect of the electronic configuration of $Cu^{II}$. The Cu6 atom exhibits a square-planar geometry with four O atoms from two $SO_4^{2-}$ and two $\mu_3$-OH groups.

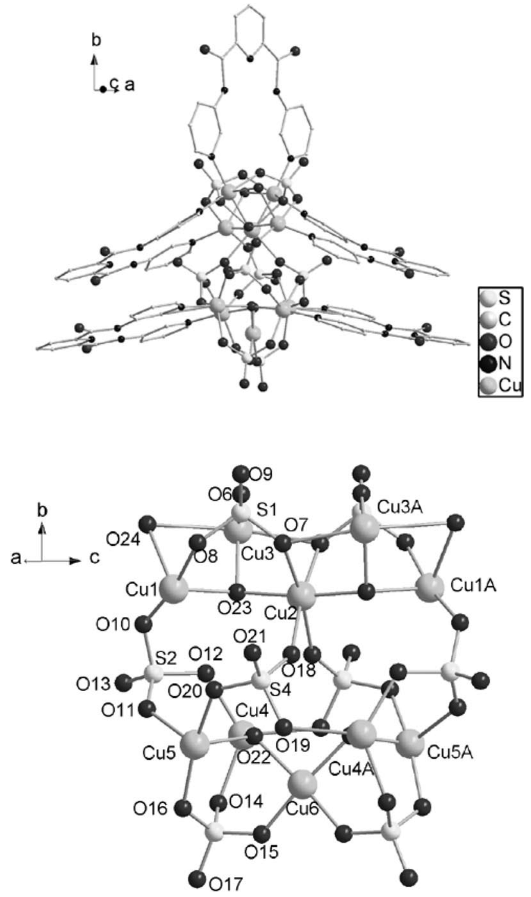


Figure 1. Molecular structure of the decanuclear copper complex **1** (top). Diamond representation of **1** emphasising the polymerisation of $[Cu_{10}]$ cages through $SO_4^{2-}$ and $\mu_3$-OH bridges (bottom).

In **1**, the five clamp-like $H_2L$ groups, polydentate in nature, form a "coordination pocket" arising from their "arms" and the copper atoms are entrapped in the "pocket" forming a $[Cu_{10}]$ cage. Moreover, each $SO_4^{2-}$ or $\mu_3$-OH group bridges three Cu atoms and plays a very decisive role in the assembly of the oxido-bridged $[Cu_{10}]$ aggregate. The Cu–O distances range from 1.901(5) to 2.366(5) Å and the neighbouring Cu···Cu distances are in the range of 3.169 to 3.610 Å.

The structure of the decacopper(II) core in **1** is different from that in the previous reports. For example, Kajiwara et al. have reported a decacopper(II) complex supported by hexaanionic *p*-(*tert*-butyl)thiacalix[6]arene.[10] The complex has a crystallographic twofold axis which divides the complex into two pentacopper(II) units and the ten coppers are connected by hydroxido, oxido and acetate groups. Abbati et al. have reported a decacopper(II) complex obtained by expansion of a hexacopper(II) cage through the addition of four $[Cu(tmpa)CN]^+$ [tmpa = tris(2-pyridylmethyl)amine] units. The complex comprises an almost planar $Cu_6$ array, plus four peripheral Cu(tmpa) units linked to the central core through cyanide bridges.[11] Recently, Yang et al. have reported a sandwich-type hexacopper(II) cage incorporating a unique hybrid hexanuclear copper complex.[12] Compared with these structures, the ten copper(II) atoms in **1** are bridged by eight$SO_4^{2-}$ groups and four $\mu_3$-OH groups. The novel oxido-bridged $[Cu_{10}]$ aggregate with rigid conjugated $H_2L$ ligands will generates unusual cooperativity or electron transfer between multimetal centres.

### Structure of $[Cu_6(L)_4(CH_3COO)_4]\cdot 2DMF\cdot 6H_2O$ (2)

Compound **2** crystallises in the space group $P\bar{1}$ and its structure features a hexanuclear copper cage (Figure 2 top). There is a crystallographic centre of inversion at the midpoint of the compound. The asymmetric unit consists of three Cu atoms, two $H_2L$ ligands and two $CH_3COO^-$ anions. Cu2 is coordinated by six donors in a slightly distorted octahedral geometry. The donors include four N atoms (N1, N5, N6, and N10) from four $H_2L$ ligands and two O atoms (O9 and O10) from water. The four rigid $H_2L$ ligands are bridged by Cu2 and Cu2A to form a cage. Cu1 is four-coordinate in a slightly distorted square planar environment by binding three N atoms (N2, N3 and N4) from one $H_2L$ ligand and one O atom (O5) from the $CH_3COO^-$ anion inside the cavity. The Cu3 atom exhibits a distorted octahedral geometry with three N atoms (N7, N8 and N9) form one $H_2L$ ligand and three O atoms (O6, O7 and O8) form two $CH_3COO^-$ anions.

These four $H_2L$ ligands form a "coordination pocket" arising from their "arms" and play a very decisive role in the assembly of the $[Cu_6]$ aggregate. Cu1, Cu1A, Cu3 and Cu3A are entrapped in the "pocket". The Cu···Cu distances in **2** are in the range of 5.831 to 9.261 Å. All the four $H_2L$ ligands in **2** are completely deprotonated which is different from in **1**. In addition, we note that the $CH_3COO^-$ anions exhibit two types of coordination mode with different conformations in this unit. One $CH_3COO^-$ anion adopts a $\mu_2$-bridging coordination mode to bridge Cu1 and Cu3 whereas the O atoms in the other $CH_3COO^-$ anion coordinate with Cu3 in a $\eta_2$-chelating coordinated mode (Figure 2, bottom).

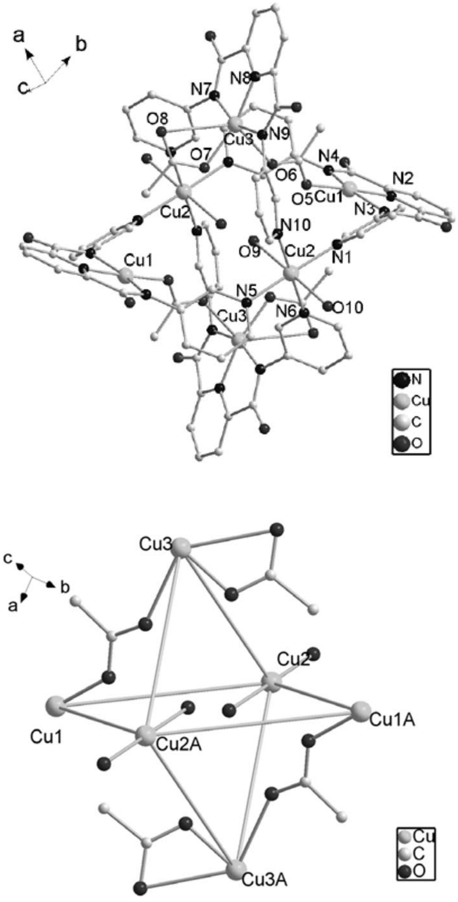


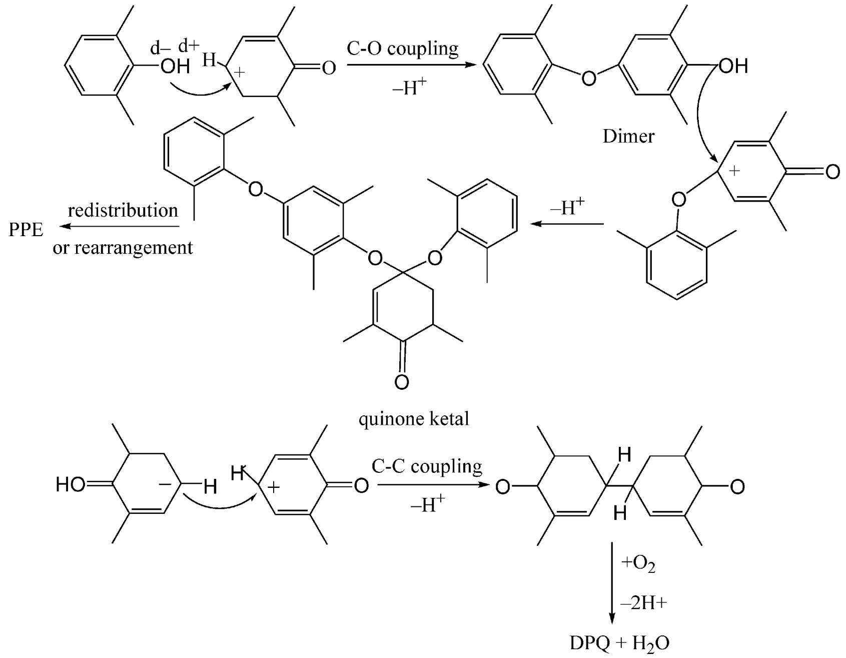
Figure 2. Molecular structure of the hexanuclear copper complex **2** (top). Diamond representation of **2** emphasising the $[Cu_6]$ cages through $OAc^-$ bridges (bottom).

### Catalytic Properties

The copper(II)-catalysed oxidative coupling of DMP in the homogeneous system has been studied intensively. After years of investigation, a two-electron transfer mechanism is now generally accepted for the phenol oxidation step of the reaction, with the formation of a dinuclear phenolate-bridged copper(II) complex as the key intermediate catalyst.[7a,13] The dinuclear phenolate-bridged species undergoes two one-electron transfers from one bridging phenolate to the copper ions resulting in a dinuclear copper(I) species and a phenoxonium cation. The cation can be attached by a phenol resulting in the formation of a bisphenol that will be oxidised to afford diphenoquinone (DPQ). Another reaction is the C–O coupling of a phenoxonium cation and a phenolate, affording dimeric phenol which may react further and will ultimately afford polymeric PPE (Scheme 2). $Cu^I$ is reoxidised to $Cu^{II}$ by dioxygen.

In order to obtain more insight into the correlations between the structural and chemical factors with the activities and selectivities of the oxidative reaction and with the objective of also optimising the catalytic polymerisation process, our interest centred on investigating the catalytic activity of complexes **1** and **2** for the oxidative coupling reaction in a heterogeneous system, ascertaining the influencing factors involved.

When DMP and a catalytic amount of **1** or **2** were stirred in a mixture of acetonitrile (5 mL) and methanol (1 mL) at room temperature under 100% dioxygen at atmospheric pressure for 24 h, PPE and DPQ are formed. As shown in



Scheme 2. Mechanistic pathways proposed for the oxidative coupling of DMP.

Table 1, we found that in acetonitrile and methanol (5:1), compounds **1** and **2** are high active heterogeneous catalysts for the coupling reaction of DMP and the reaction was selective to PPE, although there was some DPQ produced in the system. Specifically, the conversion of DMP and the PPE selectivity are 86% and 96% for **1**, and 76% and 91% for **2**, respectively (entry 3 and 9, Table 1).

Table 1. Catalytic activity of compounds **1** and **2** during the polymerisation of DMP at room temp.[a]

| Entry | Catalyst | Additive | Conversion of DMP[b] | Selectivity of PPE[c] |
|---|---|---|---|---|
| 1 | $CuCl_2$ | none | trace | |
| 2 | CuO | none | trace | |
| 3 | 1 | none | 86 | 96 |
| 4 | 1 | NaOMe[d] | 76 | 74 |
| 5 | 1 | Imidazole[e] | 87 | 95 |
| 6 | 1 | DMS[f] | 83 | 94 |
| 7 | 1 | NaOMe + imidazole | 84 | 89 |
| 8 | 1 | Imidazole + DMS | 83 | 93 |
| 9 | 2 | none | 76 | 91 |
| 10 | 2 | NaOMe | 86 | 95 |
| 11 | 2 | Imidazole | 79 | 88 |
| 12 | 2 | DMS | 72 | 87 |
| 13 | 2 | Imidazole + DMS | 77 | 85 |
| 14 | 2 | NaOMe + imidazole | 88 | 91 |
| 15 | 2 | NaOMe + imidazole + DMS | 85 | 89 |

[a] Standard conditions: DMP (1 mmol), catalyst (0.005 mmol) in $CH_3CN$ (5 mL) and $CH_3OH$ (1 mL) for 24 h under 1 atm of molecular oxygen at room temp. [b] Isolated yields, based on the amount of DMP used, average of two runs. [c] Selectivity = ([PPE] × 100)/([PPE] + [DPQ]). [d] NaOMe (0.08 mmol). [e] Imidazole (0.5 mmol). [f] DMS (2 mL).

To ascertain the influencing factors, NaOMe was added to test the influence of the basic cocatalyst on the reaction because NaOMe is believed to have the power to remove protons from the phenol substrate and thus facilitate the oxidation of the phenol in homogeneous systems.[14] Furthermore, Reedijk et al. have reported that the NaOMe and phenol can bridge two copper atoms to form a mixed μ-methoxido-μ-phenoxido-bridged dinuclear copper species, namely neocuproine which is the key intermediate of the reaction.[13a] As shown in Table 1, when NaOMe was added as the cocatalyst, the PPE selectivity decreases for both **1** and **2** and the conversion of DMP for **1** decreases. However, the conversion of DMP for **2** increases dramatically (entry 4 and 10, Table 1). This may due to the fact that, for the long Cu···Cu distance in **2**, the methoxide and phenolate may bridge two copper(II) ions from two adjacent compounds to form a dicopper species as the key reaction intermediate. However for **1**, the oxido-bridged multicopper species already exists, each dicopper species of which can be coordinated by a phenolate to form the key reaction intermediate directly. This may explain why the addition of the NaOMe exerts a favourable influence on the catalytic activity of **2** and an unfavourable influence on that of **1**.

In addition, some groups have reported that the actual mechanism involves the radical pathway with respect to the phenol coupling step in the homogeneous system. Therefore, some small heterocyclic ligands (imidazole or oxazoline) will improve the copper-catalysed oxidative coupling of DMP to PPE because they are believed to have the ability to stabilise the phenoxy radicals by forming an intermediate complex and thus facilitate the C–O coupling process.[7f] In order to check whether there are phenoxy radicals formed in the heterogeneous system, imidazole was added as a cocatalyst. However, with the addition of imidazole as the cocatalyst, there is no notable change in the conversion of DMP and the PPE selectivity in this heterogeneous system (entries 5 and 11, Table 1). These results clearly indicate that there are no phenoxy radicals formed in the presence of imidazole in the reaction. This conclusion was further verified with the use of the radical scavenger dimethyl sulfide (DMS). When the radical scavenger DMS was added, the conversion of DMP for both **1** and **2** (entries 8 and 14, Table 1) change slightly. Taking into account the fact that the addition of imidazole as a cocatalyst cannot facilitate the oxidative coupling reaction, we can deduce that the phenoxonium cations rather than phenoxy radicals seem to be very likely candidates for the key intermediate species in this heterogeneous system. The conclusion is entirely in agreement with that from the unrestricted Hartree–Fock ab initio calculations with a 6-32G* basis set.[8]

More importantly, to the best of our knowledge, compounds **1** and **2** are the first examples of heterogeneous catalysts for the oxidative coupling of DMP and show high catalytic activity with novel production-discrimination functions. We think the interesting catalytic oxidative coupling of DMP to PPE and DPQ with **1** and **2** is closely associated with their particular structural characteristics. The structure of compound **1** shows a novel decanuclear copper cage entrapped in the "coordination pocket". The ten copper atoms bridged by O atoms from $SO_4^{2-}$ and $\mu_3$-OH groups are favourable to cooperativity or electron transfer between metal centres. As far as **2** is concerned, its structure features a hexanuclear copper cage and the copper atoms are coordinatively unsaturated or coordinated with facile leaving groups ($H_2O$). The configuration of catalytic sites and the cage structure will facilitate the contact between the substances with catalytically active centres.

The remarkable advantage of the self-supported heterogeneous catalysts over their homogeneous counterparts was exemplified by the facile recovery and recycling of the catalyst. After completion of the polymerisation, simple filtration of the reaction mixture allowed the separation of the solid-state catalyst from the product-containing solution. After washing with $CHCl_3$, the isolated solids could be reused for the next run. As shown in Table 2, catalysts **1** and **2** could be used for at least four cycles in the reaction without significant loss of selectivity but at a cost of reduced activity in the last two runs. The decrease of catalytic activity can be attributed to the deposition, physisorption or chemisorption of organic substances on the surface of the catalyst.[15]

Table 2. Recycling and reuse of the heterogeneous catalysts **1** and **2** in the polymerisation of DMP.[a]

| Entry | Catalyst | % Conv.[b] | Selectivity[c] | PPE $M_w/(10^3)$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| 1 | **1** | 85 | 96 | 10.7 | 2.04 |
| 2 | **1** | 85 | 91 | 10.7 | 2.07 |
| 3 | **1** | 83 | 90 | 10.7 | 2.05 |
| 4 | **1** | 76 | 96 | 10.7 | 2.04 |
| 5 | **2** | 83 | 97 | 10.4 | 2.09 |
| 6 | **2** | 82 | 90 | 10.4 | 2.02 |
| 7 | **2** | 77 | 92 | 10.4 | 2.07 |
| 8 | **2** | 71 | 91 | 10.4 | 2.03 |

[a] All of the reactions for **1** were carried out under the reaction conditions of entry 3, Table 1. All of the reactions for **2** were carried out under the reaction conditions of entry 10, Table 1. DMP (0.5 mmol), catalyst (0.005 mmol), $CH_3CN$ (5 mL), $CH_3OH$ (1 mL), NaOMe (0.08 mmol) (for catalyst **2**), 298 K, 24 h, under 1 atm of molecular oxygen. [b] Isolated yields, based on the amount of DMP used. [c] Selectivity = ([PPE] × 100)/([PPE] + [DPQ]).

## Magnetic Properties

Magnetic susceptibility data for complex **2** were collected in the range of 300 to 1.8 K in an applied field of 2 kOe, the $\chi_M$ and $\chi_M T$ product vs. $T$ plots are depicted in Figure 3. As the system was cooled, the $\chi_M$ gradually increases and reaches a maximum of 0.13 emu mol$^{-1}$ at 6 K, below which $\chi_M$ decreases to 0.11 emu mol$^{-1}$ at 1.8 K. This is indicative of an overall antiferromagnetic coupling between the Cu$^{II}$ centres. Thus, $\chi_M T$ decreases with the lowered temperature in the whole temperature range. The $\chi_M T$ value at room temperature is 2.35 emu K mol$^{-1}$, close to the spin-only value of 2.36 emu K mol$^{-1}$ based on $Cu_6$ unit ($S_{Cu}$ = ½ and assuming $g$ = 2.05). According to the crystal structure of **2**, Cu2 is linked to Cu1 and Cu3 by the clamp-like $H_2L$ ligand which usually mediates weak magnetic coupling. While Cu1 is linked to Cu3 by acetate, so a classical dimer mode ($\boldsymbol{H} = -2J\boldsymbol{S}_1\boldsymbol{S}_2$) with additional paramagnetic Cu ions can be used in the complex and this gives the van Vleck Equation (1).

$$\chi_M = \left( \frac{2Ng^2\beta^2}{kT} \times \frac{1}{3 + e^{-2J/kT}} + \frac{Ng^2\beta^2}{3kT} S(S+1) \right) \times 2 \qquad (1)$$

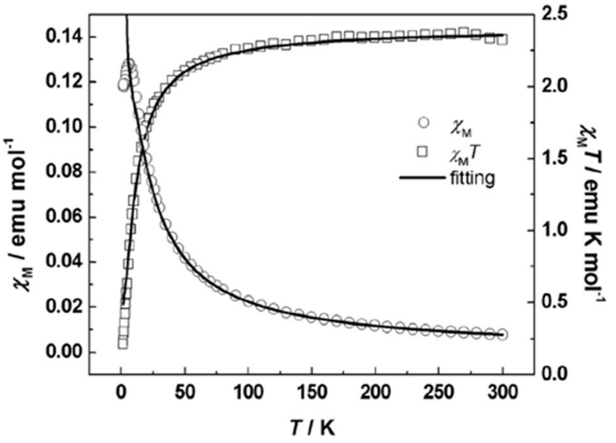


Figure 3. Plots of $\chi_M^{-1}$ vs. $T$ and $\chi_M T$ vs. $T$ for compound **2**.

When the mean-field correction was taken into account, the best fitting results gave $g$ = 2.07(1) and –6.8(4) cm$^{-1}$ (magnetic coupling between Cu2 and Cu3) and $zj'$ = –0.8(1) cm$^{-1}$ (intermolecular interaction) with $R = \Sigma[(\chi_M T)_{calc} - (\chi_M T)_{obs}]^2/\Sigma(\chi_M T)_{obs}^2 = 7.0 \times 10^{-3}$. The $J$ value indicates that weak antiferromagnetic coupling between Cu ions dominates the magnetic properties in this system.

Magnetic susceptibility data for complex **1** were also collected in the range of 300 to 1.8 K at an applied field of 2 kOe and they shows an overall antiferromagnetic coupling between the ten $Cu^{II}$ centres (Figure S1). However because of the complication of the low symmetry of compound **1**, we were unable to find a model with appropriate analytical expression for it.

The magnetic properties of **1** and **2** due to the assembly of a large number of $Cu^{II}$ ions having a $d^9$ electronic configuration in a single molecule generates unusual reactivities based on cooperativity or electron transfer between metal centres.

## Conclusions

In conclusion, we have shown that two novel high-nuclearity, discrete molecular copper(II) complexes **1** and **2** can be designed and synthesised with the use of a rigid conjugated clamp-like ligand $H_2L$. Furthermore, we have also reported for the first time that the novel discrete molecular high-nuclearity copper(II) complexes **1** and **2** are environmentally friendly, highly active heterogeneous catalysts for the polymerisation of DMP to PPE. The interesting catalytic properties of **1** and **2** are closely associated with their particular structural characteristics. In **1**, ten copper atoms are linked by five $H_2L$ ligands, eight $SO_4^{2-}$ and four $\mu_3$-OH groups to form a novel oxido-bridged [$Cu_{10}$] aggregate, thus generating unusual cooperativity or electron transfer between multimetal centres. The structure of compound **2** features a hexanuclear copper cage and the copper atoms in **2** are coordinatively unsaturated or coordinated with facile leaving groups which facilitate the contact between the substances with catalytically active centres. These catalysts could be easily recovered by a simple filtration and used repeatedly. These catalysts, when used for the polymerisation of DMP, appear to be efficient, mild and easily recyclable.

## Experimental Section

**Materials and Physical Techniques:** All chemicals were of reagent-grade quality obtained from commercial sources and were used without further purification. $H_2L$ was prepared by literature methods.[16] IR data were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer with KBr pellets in the 400–4000 $cm^{-1}$ region. UV/Vis spectra were obtained on an HP 8453 spectrophotometer. NMR spectra were recorded on a Bruker DPX-400 spectrometer. Elemental analyses (C, H and N) were carried out with a FLASH EA 1112 analyser. Molecular weights of the PPE were determined on a Waters 150C gel permeation chromatography (GPC) instrument. Magnetic susceptibility data were obtained on a microcrystalline sample using a Quantum Design MPMS-XL7 SQUID magnetometer.

**Preparation of Complex 1:** The ligand $H_2L$ (0.05 mmol, 0.016 g) in DMF (5 mL) was added dropwise to a solution of $CuSO_4 \cdot 5H_2O$ (0.1 mmol, 0.025 g) in alcohol (3 mL). The precipitate was filtered and the resultant green solution was allowed to stand at room temperature in the dark. After one week green crystals were obtained which were further used for single-crystal analysis and physical measurements. Yield 21.8 mg (64%) based on Cu. $C_{93}H_{111}Cu_{10}N_{25}O_{59}S_8$ (3414.952): calcd. C 32.71, H 3.28, N 10.25, S 7.51; found C 32.48, H 3.35, N 10.11, S 7.47. IR data (KBr): $\tilde{\nu}$ = 3435 [s ν(N–H)], 3183 [m ν(C–H)], 1624 [m ν(C=O)], 1546 [w ν(Py)], 1484 [w ν(Py)], 1399 [s ν(C–N)], 1125 [s δ(Py–H)], 619 [m δ(Py–H)] $cm^{-1}$.

**Preparation of Complex 2:** The ligand $H_2L$ (0.05 mmol, 0.016 g) in DMF (5 mL) was added dropwise to a solution of $Cu(OAc)_2$ (0.1 mmol, 0.020 g) in methanol (3 mL). The precipitate was filtered and the resultant green solution was allowed to stand at room temperature in the dark. After one week good quality dark-green crystals were obtained and dried in air. Yield 26.8 mg (75%) based on Cu. $C_{41}H_{41}Cu_3N_{11}O_{12}$ (1070.47): calcd. C 46.00, H 3.83, N 14.39; found C 46.73, H 3.85, N 14.77. IR data (KBr): $\tilde{\nu}$ = 3425 [s ν(NH)], 2364 (w), 1583 [s ν(Py)], 1483 [w ν(Py)], 1426 [w ν(Py)], 1386 [w ν(C–N)], 1114 [s δ(Py–H)], 700 [w δ(Py–H)], 653 [m δ(Py–H)], 620 [m δ(Py–H)] $cm^{-1}$.

Both complexes **1** and **2** are insoluble in common organic solvent such as MeOH, EtOH, MeCN and THF but are only very slightly soluble in highly polar solvents such as dimethylsulfoxide (DMSO) and dimethylformamide (DMF).

**A Typical Procedure for the Oxidative Coupling Polymerisation of 2,6-Dimethylphenol:** A solution of NaOMe (0.004 g, 0.08 mmol) in methanol (1 mL) was added to a solution of DMP (0.122 g, 1 mmol) in acetonitrile (5 mL). The solid-state catalyst (0.005 mmol) was added to the solution and the resultant heterogeneous mixture was stirred vigorously in oxygen at room temperature for 24 h. The mixture was then diluted with chloroform (50 mL). After the isolation of the solid-state catalyst by filtration, the filtrate was put into 100 mL measuring flask.

In addition, we analysed the filtrate by atom adsorption and the results showed that there was a tiny amount of $Cu^{II}$ ions (ca. $10^{-4}$ M) in the filtrate. The filtrate could not catalyse the reaction and, as a result, the catalytic activities observed are not due to the “soluble” copper ions.

UV/Vis spectroscopic detection of DPQ: a 1 mL sample was removed and diluted with chloroform. This solution gave a UV/Vis absorption with a maximum at 421 nm which was ascribed to DPQ. The molar extinction coefficient $\varepsilon$ was determined in chloroform using pure DPQ. The amount of formed DPQ is given as a percentage of the feed amount of DMP.

The filtrate was concentrated and the residue was submitted to layer chromatography on silica gel with petroleum ether/ethyl acetate (4:1) as the mobile phase to give the PPE as an off-white solid. We could also get the polymeric materials by a reprecipitation procedure (chloroform as solvent, methanol as cosolvent). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.10 (s, 6 H, $CH_3$), $\delta$ = 6.45 (s, 2 H, $H_{Ar}$) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 16.8 ($CH_3$), 114.5 (CH), 132.7 (C), 145.6 (C), 154.5 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3429 (m), 2922 (w), 1607 (s), 1471 (s), 1306 (s), 1189 (s), 1022 (s), 858 (m) $cm^{-1}$.

The insoluble catalyst was washed with chloroform and dried for the next run. The elemental analyses on the filtered catalysts after reaction revealed the same compositions as the original catalysts. Elemental analysis (%) after catalytic reaction for **1**: $C_{93}H_{111}Cu_{10}N_{25}O_{59}S_8$: found C 32.51, H 3.19, N 10.45, S 7.39. For **2**: $C_{41}H_{41}Cu_3N_{11}O_{12}$: found C 46.61, H 3.77, N 14.59.

**Structure Determination:** Suitable single crystals with dimensions of 0.20 × 0.18 × 0.17 mm for **1** and 0.22 × 0.15 × 0.11 mm for **2** were selected for single-crystal X-ray diffraction analysis. Data collection was performed on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) at room temperature. The numbers of collected and observed independent [$I > 2\sigma(I)$] reflections are 37667 and 14475 ($R_{int}$ = 0.089) for **1**, and 13037 and 8613 ($R_{int}$ = 0.061) for **2**. The data were integrated using the Siemens SAINT program. Absorption corrections were applied. The structures were solved by direct methods and refined on $F^2$ by using full-matrix least-squares in SHELXTL.[17] Crystallographic and refinement details are listed in Table 3 with selected bond lengths and angles given in Tables 4 and 5.

Table 3. Crystal and structure refinement data for complexes **1** and **2**.

| Compounds | 1 | 2 |
|---|---|---|
| Formula | $C_{93}H_{111}Cu_{10}N_{25}O_{59}S_8$ | $C_{41}H_{41}Cu_3N_{11}O_{12}$ |
| Formula weight | 3414.952 | 1070.47 |
| Space group | *C*2/*c* | $P\bar{1}$ |
| *a* [Å] | 33.22(2) | 13.7000(14) |
| *b* [Å] | 21.673(15) | 14.1454(14) |
| *c* [Å] | 25.820(18) | 14.6372(14) |
| *α* [°] | 90.00 | 85.813(2) |
| *β* [°] | 116.971(11) | 72.453(2) |
| *γ* [°] | 90.00 | 67.187(2) |
| *V* [Å³] | 16567(20) | 2489.9(4) |
| *Z* | 4 | 2 |
| $\rho_{calcd.}$ [Mg m$^{-3}$] | 1.368 | 1.428 |
| Temperature [K] | 273(2) | 273(2) |
| $\lambda$(Mo-$K_\alpha$) [Å] | 0.71073 | 0.71073 |
| Final $R_1$,[a] $wR_2$[b] | 0.0898, 0.2326 | 0.0609, 0.1680 |
| *R* indices (all data) | 0.2278, 0.2641 | 0.0958, 0.1870 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$. $w = 1/[\sigma^2(F_o)^2 + 0.0297P^2 + 27.5680P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 4. Selected bond lengths [Å] and angles [°] for **1**.[a]

| | | | |
|---|---|---|---|
| O(6)–Cu(3) | 1.990(7) | O(7)–Cu(2) | 2.176(7) |
| O(7)–Cu(3)#1 | 2.366(7) | O(8)–Cu(1) | 1.963(7) |
| O(10)–Cu(1) | 1.972(8) | O(11)–Cu(5) | 2.172(7) |
| O(12)–Cu(4) | 2.041(7) | O(14)–Cu(4) | 2.033(8) |
| O(15)–Cu(6) | 1.901(8) | O(16)–Cu(5) | 1.995(7) |
| O(18)–Cu(2) | 2.172(7) | O(19)–Cu(4) | 2.200(7) |
| O(20)–Cu(5)#1 | 1.964(7) | O(22)–Cu(4) | 1.998(7) |
| O(22)–Cu(6) | 1.998(6) | O(22)–Cu(5) | 2.025(6) |
| O(23)–Cu(2) | 2.000(6) | O(23)–Cu(1) | 2.021(6) |
| O(23)–Cu(3) | 2.047(7) | O(24)–Cu(1) | 2.345(9) |
| N(1)–Cu(3)#1 | 2.004(9) | N(10)–Cu(5)#1 | 2.003(9) |
| N(5)–Cu(1) | 2.016(9) | N(6)–Cu(4) | 2.003(9) |
| N(11)–Cu(3) | 2.041(11) | Cu(2)–O(23)#1 | 2.000(6) |
| Cu(2)–O(18)#1 | 2.172(7) | Cu(2)–O(7)#1 | 2.176(8) |
| Cu(3)–N(1)#1 | 2.004(9) | Cu(3)–O(7)#1 | 2.366(7) |
| Cu(5)–O(20)#1 | 1.964(7) | Cu(5)–N(10)#1 | 2.003(8) |
| Cu(6)–O(15)#1 | 1.901(8) | Cu(6)–O(22)#1 | 1.998(6) |
| O(8)–Cu(1)–O(10) | 168.6(3) | O(8)–Cu(1)–N(5) | 90.0(4) |
| O(10)–Cu(1)–N(5) | 93.3(4) | O(8)–Cu(1)–O(23) | 92.3(3) |
| O(10)–Cu(1)–O(23) | 90.2(3) | N(5)–Cu(1)–O(23) | 150.9(3) |
| O(8)–Cu(1)–O(24) | 87.9(3) | O(10)–Cu(1)–O(24) | 80.8(3) |
| N(5)–Cu(1)–O(24) | 116.0(4) | O(23)–Cu(1)–O(24) | 93.1(3) |
| O(23)–Cu(2)–O(23)#1 | 173.2(4) | O(23)–Cu(2)–O(18)#1 | 100.6(3) |
| O(23)#1–Cu(2)–O(18)#1 | 84.6(3) | O(23)–Cu(2)–O(18) | 84.6(3) |
| O(23)#1–Cu(2)–O(18) | 100.6(3) | O(18)#1–Cu(2)–O(18) | 81.8(4) |
| O(23)–Cu(2)–O(7) | 91.3(3) | O(23)#1–Cu(2)–O(7) | 84.0(3) |
| O(18)#1–Cu(2)–O(7) | 92.2(3) | O(18)–Cu(2)–O(7) | 171.9(3) |
| O(23)–Cu(2)–O(7)#1 | 84.0(3) | O(6)–Cu(3)–N(11) | 88.1(4) |
| O(6)–Cu(3)–O(23) | 89.4(3) | N(11)–Cu(3)–O(23) | 175.6(3) |
| O(22)–Cu(4)–N(6) | 174.9(3) | O(22)–Cu(4)–O(14) | 90.8(3) |
| N(6)–Cu(4)–O(14) | 87.5(3) | O(22)–Cu(4)–O(12) | 88.6(3) |
| N(6)–Cu(4)–O(12) | 96.2(3) | O(14)–Cu(4)–O(12) | 128.5(3) |
| O(22)–Cu(4)–O(19) | 83.2(3) | N(6)–Cu(4)–O(19) | 93.1(4) |
| O(14)–Cu(4)–O(19) | 115.4(3) | O(12)–Cu(4)–O(19) | 115.6(3) |
| O(16)–Cu(5)–O(22) | 90.6(3) | O(16)–Cu(5)–O(11) | 92.5(3) |
| O(22)–Cu(5)–O(11) | 95.9(3) | O(15)–Cu(6)–O(22) | 90.0(3) |

[a] Symmetry transformations used to generate equivalent atoms: #1 – *x*, *y*, –*z* + ½

Table 5. Selected bond lengths [Å] and angles [°] for **2**.[a]

| | | | |
|---|---|---|---|
| N(1)–Cu(2) | 2.028(4) | N(3)–Cu(1) | 1.924(5) |
| N(4)–Cu(1) | 2.006(5) | N(5)–Cu(2)#1 | 2.049(4) |
| N(6)–Cu(2) | 2.029(4) | N(7)–Cu(3) | 2.017(4) |
| N(8)–Cu(3) | 1.930(4) | N(9)–Cu(3) | 2.008(4) |
| N(10)–Cu(2)#1 | 2.018(4) | O(5)–Cu(1) | 1.904(4) |
| O(7)–Cu(3) | 1.947(4) | Cu(2)–N(10)#1 | 2.018(4) |
| Cu(2)–N(5)#1 | 2.049(4) | O(5)–Cu(1)–N(4) | 100.61(19) |
| O(5)–Cu(1)–N(3) | 176.4(2) | N(3)–Cu(1)–N(4) | 80.5(2) |
| O(5)–Cu(1)–N(2) | 98.66(19) | N(3)–Cu(1)–N(2) | 80.1(2) |
| N(4)–Cu(1)–N(2) | 160.57(19) | N(10)#1–Cu(2)–N(1) | 90.29(18) |
| N(10)#1–Cu(2)–N(6) | 179.52(18) | N(1)–Cu(2)–N(6) | 89.25(18) |
| N(10)#1–Cu(2)–N(5)#1 | 90.05(18) | N(1)–Cu(2)–N(5)#1 | 177.81(18) |
| N(6)–Cu(2)–N(5)#1 | 90.41(17) | N(8)–Cu(3)–O(7) | 164.24(19) |
| N(8)–Cu(3)–N(9) | 79.19(18) | O(7)–Cu(3)–N(9) | 100.33(18) |
| N(8)–Cu(3)–N(7) | 79.90(17) | O(7)–Cu(3)–N(7) | 99.40(17) |
| N(9)–Cu(3)–N(7) | 159.04(18) | | |

[a] Symmetry transformations used to generate equivalent atoms: #1 –*x* + 1, –*y* + 1, –*z* + 2.

CCDC-640706 (for **1**) and -640707 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif..

**Supporting Information** (see also the footnote on the first page of this article): Crystallographic and refinement details for **1** and **2**. Plots of $\chi_M^{-1}$ vs. *T* and $\chi_M T$ vs. *T* for compound **1**.

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[1] a) S. Itoh, in *Comprehensive Coordination Chemistry*, vol. 8 (Eds.: J. A. McCleverty, T. J. Meyer, L. Que, W. B. Tolman), 2nd ed., Elsevier, Dordrecht, **2003**, chapter 8.15, pp. 369–393; b) P. Chen, S. I. Gorelsky, S. Ghosh, E. I. Solomon, *Angew. Chem. Int. Ed.* **2004**, *43*, 4132–4140; c) E. I. Solomon, U. M. Sundaram, T. E. Machonkin, *Chem. Rev.* **1996**, *96*, 2563–2605.

[2] a) G. Aromí, J. Ribas, P. Gamez, O. Roubeau, H. Kooijman, A. L. Spek, S. Teat, E. Maclean, H. Stoeckli-Evans, J. Reedijk, *Chem. Eur. J.* **2004**, *10*, 6476–6488; b) X. Ottenwaelder, J. Cano, Y. Journaux, E. Rivière, C. Brennan, M. Nierlich, R. Ruiz-García, *Angew. Chem. Int. Ed.* **2004**, *43*, 850–852; c) A. Mukherjee, M. Nethaji, A. R. Chakravarty, *Angew. Chem. Int. Ed.* **2004**, *43*, 87–90; d) G. Aromí, P. Gamez, O. Roubeau, H. Kooijman, A. L. Spek, W. L. Driessen, J. Reedijk, *Angew. Chem. Int. Ed.* **2002**, *41*, 1168–1170; e) A. Mukherjee, R. Raghunathan, M. K. Saha, M. Nethaji, S. Ramasesha, A. R. Chakravarty, *Chem. Eur. J.* **2005**, *11*, 3087–3096.

[3] S. Dehnen, A. Eichhöfer, D. Fenske, *Eur. J. Inorg. Chem.* **2002**, 279–317.

[4] For examples: a) M. Murugesu, C. E. Anson, A. K. Powell, *Chem. Commun.* **2002**, 1054–1055; b) R. Wegner, M. Gottschaldt, H. Görls, E.-G. Jäger, D. Klemm, *Chem. Eur. J.* **2001**, *7*, 2143–2157; c) V. Chandrasekhar, L. Nagarajan, K. Gopal, V. Baskar, P. Kögerler, *Dalton Trans.* **2005**, 3143–3145; d) C.-H.

Chang, K. C. Hwang, C.-S. Liu, Y. Chi, A. J. Carty, L. Scoles, S.-M. Peng, G.-H. Lee, J. Reedijk, *Angew. Chem. Int. Ed.* **2001**, *40*, 4651–4653; e) N. Kon, N. Iki, T. Kajiwara, T. Ito, S. Miyani, *Chem. Lett.* **2006**, *35*, 430–431; f) L. Zhao, Z.-Q. Xu, L. K. Thompson, S. L. Heath, D. O. Miller, M. Ohba, *Angew. Chem. Int. Ed.* **2000**, *39*, 3114–3117; g) V. Pashchenko, B. Brendel, B. Wolf, M. Lang, K. Lyssenko, O. Shchegolikhina, Y. Molodtsova, L. Zherlitsyna, N. Auner, F. Schütz, M. Kollar, P. Kopietz, N. Harrison, *Eur. J. Inorg. Chem.* **2005**, 4617–4625; h) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, P. Kögerler, C. Rosu, E. Beckman, *Angew. Chem. Int. Ed.* **2001**, *40*, 4034–4037; i) A. L. Keen, M. Doster, H. Han, S. A. Johnson, *Chem. Commun.* **2006**, 1221–1223; j) Y. Bai, G. He, Y. Zhao, C. Duan, D. Dang, Q. Meng, *Chem. Commun.* **2006**, 1530–1532; k) S. Triki, F. Thétiot, J. S. Pala, S. Golhen, J. M. Clemente-Juan, C. J. Gómez-García, E. Coronado, *Chem. Commun.* **2001**, 2172–2173.

[5] a) G. F. Manbeck, A. J. Lipman, R. A. Stockland Jr, A. L. Freidl, A. F. Hasler, J. J. Stone, I. A. Guzei, *J. Org. Chem.* **2005**, *70*, 244–250; b) A. M. Kirillov, M. N. Kopylovich, M. V. Kirillova, M. Haukka, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Angew. Chem. Int. Ed.* **2005**, *44*, 4345–4349; c) A. M. Kirillov, M. N. Kopylovich, M. V. Kirillova, E. Y. Karabach, M. Haukka, M. F. C Guedes da Silva, A. J. L. Pombeiro, *Adv. Synth. Catal.* **2006**, *348*, 159–174; d) G. A. Ardizzoia, M. A. Angaroni, G. L. Monica, F. Cariati, S. Cenini, M. Moret, N. Masciocchi, *Inorg. Chem.* **1991**, *30*, 279–317; e) M. Zaręba, M. Legięć, B. Sanecka, J. Sobczak, M. Hojniak, S. Wołowiec, *J. Mol. Catal. A* **2006**, *248*, 144–147; f) C. D. Nicola, Y. Y. Karabach, A. M. Kirillov, M. Monari, L. Pandolfo, C. Pettinari, A. J. L. Pombeiro, *Inorg. Chem.* **2007**, *46*, 221–230; g) P. Roy, K. Dhara, M. Manassero, P. Banerjee, *Eur. J. Inorg. Chem.* **2008**, 4404–4412.

[6] P. Roy, K. Dhara, M. Manassero, P. Banerjee, *Inorg. Chem. Commun.* **2008**, *11*, 265–269.

[7] For examples: a) P. J. Baesjou, W. L. Driessen, G. Challa, J. Reedijk, *Macromolecules* **1999**, *32*, 270–276; b) K. Saito, T. Tago, T. Masuyama, H. Nishide, *Angew. Chem. Int. Ed.* **2004**, *43*, 730–733; c) P. Gamez, C. Simons, G. Aromí, W. L. Driessen, G. Challa, J. Reedijk, *Appl. Catal. A* **2001**, *214*, 187–192; d) R. Ikeda, J. Sugihara, H. Uyama, S. Kobayashi, *Macromolecules* **1996**, *29*, 8702–8705; e) H. Nishino, H. Satoh, M. Yayumi, K. Kurosawa, *J. Chem. Soc. Perkin Trans. 2* **1999**, 1919–1924; f) J. Gao, S.-H. Zhong, R. A. Zingaro, *J. Mol. Catal. A* **2004**, *207*, 15–20; g) M. Huisman, I. A. Koval, P. Gamez, J. Reedijk, *Inorg. Chim. Acta* **2006**, *359*, 1786–1794; h) J. Gao, J. H. Reibenspies, A. E. Martell, *Inorg. Chim. Acta* **2002**, *338*, 157–164; i) C. Boldron, G. Aromí, G. Challa, P. Gamez, J. Reedijk, *Chem. Commun.* **2005**, 5808–5810; j) A. Camus, M. S. Garozzo, N. Marsich, M. Mari, *J. Mol. Catal. A* **1996**, *112*, 353–365.

[8] A. S. Hay, H. S. Stofford, G. F. Endres, J. W. Eustance, *J. Am. Chem. Soc.* **1995**, *81*, 6335–6336.

[9] a) B. Xiao, H.-W. Hou, Y.-T. Fan, *J. Organomet. Chem.* **2007**, *692*, 2014–2020; b) B. Xiao, H.-W. Hou, Y.-T. Fan, *J. Mol. Catal. A* **2008**, *288*, 42–51; c) E.-P. Zhang, H.-W. Hou, H.-Y. Han, Y.-T. Fan, *J. Organomet. Chem.* **2008**, *693*, 1927–1937.

[10] T. Kajiwara, N. Kon, S. Yokozawa, T. Ito, N. Iki, S. Miyano, *J. Am. Chem. Soc.* **2002**, *124*, 11274–11275.

[11] G. L. Abbati, A. Caneschi, A. Cornia, A. C. Fabretti, Y. A. Pozdniakova, O. I. Shchegolikhina, *Angew. Chem. Int. Ed.* **2002**, *41*, 4517–4520.

[12] S.-T. Zheng, D.-Q. Yuan, J. Zhang, G.-Y. Yang, *Inorg. Chem.* **2007**, *46*, 4569–4574.

[13] a) C. Boldron, P. Gamez, D. M. Tooke, A. L. Spek, J. Reedijk, *Angew. Chem. Int. Ed.* **2005**, *44*, 3585–3587; b) J. Kresta, A. Tkac, R. Prikryl, L. Malik, *Makromol. Chem.* **1975**, *176*, 157–175.

[14] P. J. Baesjou, W. L. Driessen, G. Challa, J. Reedijk, *J. Mol. Catal. A* **1996**, *110*, 195–210.

[15] J. M. Thomas, W. J. Thomas, *Principles and Practice of Heterogeneous Catalysis*, Wiley-VCH, Weinheim, Germany, **1997**.

[16] Z.-Q. Qin, M. C. Jennings, R. J. Puddephatt, *Inorg. Chem.* **2003**, *42*, 1956–1965.

[17] a) G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, Göttingen University, Germany, **1997**; b) G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, Göttingen University, Germany, **1997**.

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