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Structure and catalytic activity of a hexarhenium cluster-supported copper cubanes $[\{Cu_4(\mu\text{-}OH)_4(NH_3)_7\}_2\{Re_6Se_8(CN)_6\}][Re_6Se_8(CN)_6] \cdot 2H_2O$

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Abstract

The first hexarhenium cluster-supported $Cu_4(OH)_4$ cubanes had been synthesized. The complex displayed a belt-like one-dimensional structure with dangling Cu_4 cubanes. As a heterogeneous catalyst, the complex showed a high catalytic activity in the transesterification of a range of esters with methanol under the mild conditions. Moreover, it can be reused without any loss of activity through five runs with ester, which suggests that this catalyst is an efficient, mild, and easily recyclable one for the alcoholysis of esters.

Keywords: Cyano-bridged hexarhenium cluster; Crystal structure; Transesterification; Catalytic activity

The soluble cyano-hexarhenium clusters $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se, Te) have been used as molecular building blocks in crystal engineering or developing supporting materials for catalysts [1]. In solid frameworks, metal cations bridge the Re_6 clusters *via* six cyanide groups forming large cubical cavities which can include plenty of small solvent molecules as well as metal ions [1]. We have previously prepared polymeric materials: 2D framework $[Mn(salen)]_{4n}[Re_6Te_8(CN)_6]_n$ [2] and 3D framework $Na[Mn(salen)_3][Re_6Se_8(CN)_6]$ [3], and also reported Re_6 cluster-supported manganese(III) porphyrin: $[Mn(OEP)]_4$-$[Re_6Te_8(CN)_6]$ (OEP = octaethylporphinato dianion), $[Mn(TPP)]_4[Re_6Te_8(CN)_6]$ (TPP = tetraphenylporphinato dianion) [4], in which, $[Mn(TPP)]_4[Re_6Te_8(CN)_6]$ showed a high catalytic activity in the epoxidation of olefins by iodosylbenzene, and Re_6 cluster-supported iridium(I) compound $[Re_6Te_8\{CNIr(CO)(PPh_3)_2\}_6]$, which is effective in catalyzing hydrogenation [5].

Since copper has recently gained prominence as a catalyst for numerous transformations [6], we have planned to attach cubane units $[Cu_4(OH)_4(NH_3)_7]^{4+}$ to cyano-hexarhenium clusters $[Re_6Se_8(CN)_6]^{4-}$ to produce a new hexarhenium cluster-supported catalyst for the heterogeneous catalytic reactions. Here we report first Re_6 cluster-supported copper cubanes: $[\{Cu_4(\mu\text{-}OH)_4(NH_3)_7\}_2\{Re_6Se_8(CN)_6\}][Re_6Se_8(CN)_6] \cdot 2H_2O$ (**1**), where cupper units $Cu_4(\mu\text{-}OH)_4(NH_3)_7$ are linked to the cyano-rhenium clusters to form a polymeric belt-like inorganic extended framework with novel catalytic transesterification activity.

$[\{Cu_4(OH)_4(NH_3)_7\}_2\{Re_6Se_8(CN)_6\}][Re_6Se_8(CN)_6] \cdot 2H_2O$ (**1**) was prepared by a direct diffusion technique in which an aqua solution of $[Cu(NH_3)_4SO_4]$ was carefully

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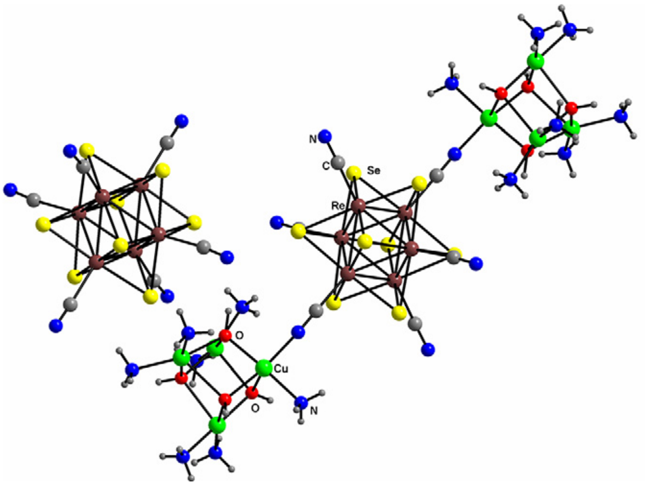

Fig. 1. The structure of compound **1**.

layered with an aqua solution of $K_4[Re_6Se_8(CN)_6]$ cluster.[1] The structure of the compound was solved by X-ray single-crystal analysis.[2]

The asymmetric unit contains two half of a Re cluster, a cubane unit $[Cu_4(OH)_4(NH_3)_7]^{4+}$, and a water solvent molecule. The complete structure is generated by the symmetry operations $(-x+2, -y+1, -z+1)$ and $(-x+2, -y+1, -z)$. Two cyano groups of the cluster in *trans* directions (C–N distance of 1.15(2) Å) are connected to two copper atoms from two different cubane units $[Cu_4(OH)_4(NH_3)_7]^{4+}$, and the other four cyano groups with C–N distances of 1.12(2) and 1.18(2) Å remain dangling (Fig. 1). Another isolated Re6 cluster keeps the charge balance. The IR spectrum of **1** had two $C\equiv N$ stretching peaks at 2109 and 2151 cm^{-1}, which shows two different types of cyano groups: bridging and terminal ones. This result is consistent with the X-ray crystallographic data. In cubane units, four Cu(II) atoms and four hydroxyl oxygen atoms occupy the alternative vertices of the cubane. One of four Cu(II) ions in a cubane is linked by a cyano group of the Re6 cluster, and also coordinated by one ammonia and three hydroxyl groups. The other three Cu(II) ions are coordinated by three hydroxyl groups and two ammonia molecules. The coordination geometry of each Cu(II) ion is best described as a distorted square pyramid with two hydroxyl oxygen and two ammonia nitrogen atoms (Cu–O/N mean distance of 2.0 Å) in the plane and one hydroxyl oxygen atom (Cu–O mean distance of 2.2 Å) on the apical position. An extended belt-like structure (Fig. 2) is formed through intermolecular Cu···N interactions (The distance of Cu···N($x, -1+y, z$) is 2.697(2) Å).

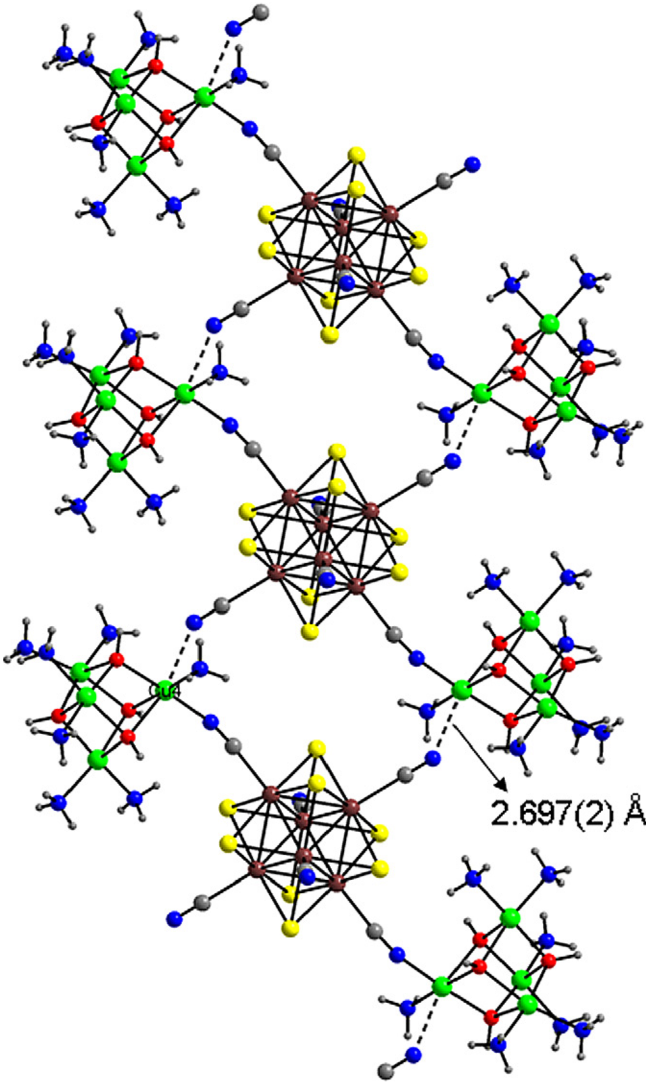

Fig. 2. The belt-like one-dimensional structure with intermolecular Cu…N interactions (the distance of Cu–N($x, -1+y, z$) is 2.697(2) Å) shown in dotted lines.

In our compound **1**, $Cu_4(\mu\text{-}OH)_4$ was coordinated to the octahedral metal-chalcogenide cluster $[Re_6Se_8(CN)_6]^{4-}$ that is the first hexarhenium cluster-supported Cu_4 cubanes. The $Cu_4(\mu\text{-}OH)_4$ core in compound **1** is similar to that in the previously reported compound $[Cu_4(\mu\text{-}OH)_4][Re_4Te_4(CN)_{12}]$ (**2**). The geometrical environment of the cluster anion $[Re_6Se_8(CN)_6]^{4-}$ is similar to that previously reported [7]. The cubane-like $Cu_4(\mu\text{-}OH)_4$ fragment

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[1] Preparation of single crystals of **1**: the single crystals of **1** were prepared by a direct diffusion technique in which H_2O solution of $[Cu(NH_3)_4SO_4]$ was carefully layered with a H_2O solution of $K_4[Re_6Se_8(CN)_6]$ complex. During preparing $[Cu(NH_3)_4SO_4]$, the stoichiometric amount of ammonia was added dropwise to a stirred solution of $CuSO_4 \cdot 5H_2O$ until pale blue precipitation disappeared. The bulk material of **1** was tried to be prepared by mixing a H_2O solution of $[Cu(NH_3)_4SO_4]$ and H_2O solution of $K_4[Re_6Se_8(CN)_6]$, and the result was confirmed by powder X-ray diffraction data. Anal. Calc. for $C_{12}H_{54}Cu_8N_{26}O_{10}Re_{12}Se_{16}$ (4728.9): C, 3.05; H, 1.15, N, 7.70. Found: C, 3.11; H, 1.09; N, 7.68%.

[2] Crystal data for $[\{Cu_4(OH)_4(NH_3)_7\}_2\{Re_6Se_8(CN)_6\}][Re_6Se_8(CN)_6]\cdot 2H_2O$ (**1**): $C_{12}H_{54}Cu_8N_{26}O_{10}Re_{12}Se_{16}$ (M = 4728.9), triclinic space group, $P\bar{1}$, $a = 9.367(4)$ Å, $b = 10.025(4)$ Å, $c = 19.910(7)$ Å, $\alpha = 93.298(7)$, $\beta = 100.742(7)$, $\gamma = 97.518(7)$, $V = 1814.7(12)$ Å^3, $Z = 1$, $d_{calc} = 4.327$ g/cm^3, 10136 reflections measured, 6941 unique ($R_{int} = 0.0369$) which were used in all calculations, final $R = 0.0479$ ($R_w = 0.0974$) with reflections having intensities greater than 2σ, GOF = 0.916.

was reported previously in three complexes [8], but only in one compound $[Cu_4(\mu\text{-}OH)_4][Re_4Te_4(CN)_{12}]$ **2**, $Cu_4(\mu\text{-}OH)_4$ core was connected to the cluster. In this previously reported compound **2**, $Cu_4(\mu\text{-}OH)_4$ was linked to a metal-chalcogen cubane cluster $[Re_4Te_4(CN)_{12}]^{4-}$ through cyanide groups. The coordination numbers of Cu(II) in **1** and **2** are all 5, and the distortions of $Cu_4(\mu\text{-}OH)_4$ from ideal cubic geometry in **1** and **2** are almost the same (The mean band distances of Cu···Cu are 3.054 Å and 3.257 Å in **1**, and those in **2** are 2.99 Å and 3.18 Å). The coordination geometry of Cu(II) ion of our compound **1** is a distorted square pyramid similar to the previously reported compound **2**. In our compound **1**, Cu(II) ions are linked by ammonia molecules besides cyano groups, but Cu(II) ions in compound **2** are coordinated only by cyano groups. The main difference between our compound **1** and the previously reported compound **2** is that compound **1** show a one-dimensional belt-like structure, and the compound **2** show a two-dimensional layered structure.

Since copper has recently gained prominence as a catalyst for numerous transformations [6] and heterogeneous catalysts are easy to handle and separate from the reaction solution [9], we have examined the reactivity of the compound **1** as a potential heterogeneous catalyst for the transesterification reaction under mild conditions. The compound **1**, which was ground well into appropriate sizes for high surface area but not too small for a convenient filtration [10], was treated with *p*-nitrophenyl acetate and methanol in the presence of **1** at 50 °C under the neutral conditions (Eq. (1)) [11]. This reaction, surprisingly, produced quantitatively the corresponding product methyl acetate within 3 days (entry 1 of Table 1; see the supplementary information for the detailed reaction conditions), while a control reaction carried out in absence of the catalyst **1** showed trace amounts of the conversion of the ester to the product in the same time period. To the best of our knowledge, this is the first report on the use of the hexarhenium cluster-supported copper compound for the heterogeneous transesterification reaction.

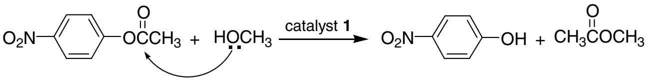
Table 1
Transesterfication of esters by methanol in the presence of the compound **1** at 50 °C[a]

Entry	Substrate	1 (Time/day)	Yield[b]
1	4-Nitrophenyl acetate	3	100
2	4-Fluorophenyl acetate	24	100
3	Phenyl acetate	13	100
4	4-Nitrophenyl benzoate[c]	10	100
5	4-Chlorophenyl benzoate	10	100
6	Phenyl benzoate	10	100
7	Vinyl acetate	2	100

[a] All esters were completely converted to the corresponding product by methanol. See the supplementary information for the detailed reaction conditions.

[b] Based upon the products, methyl acetate or methyl benzoate.

[c] The solvent was a mixture of CH_3OH/CH_3CN (1/1) because of low solubility of substrate in CH_3OH.



(1)

The potential benefits of the heterogeneous catalyst include facilitation of catalyst separation from reagents and reaction products, and simplification of methods for catalyst recycle [9]. For a truly effective heterogeneous catalyst, therefore, it is critical that recovery could be simple and efficient, and that the recovered catalyst could retain its original reactivity through multiple cycles. As the polymeric compound **1** showed adequate activity, we tested for its recovery and reuse. After the reaction completed, the catalyst was recovered by filtration and thoroughly washed with methanol for the consecutive runs. The recovered catalyst was used for a new reaction batch of *p*-nitrophenyl acetate. The catalyst **1** showed excellent reusability for 5 times without showing any significant deterioration of catalytic activity (see Table S1 of the supplementary information).

Then, we have carried out another control reaction before further reactivity study with other substrates, because in the catalytic process the leached metal species might catalyze efficiently the transesterification reaction instead of the heterogeneous catalysts [10]. To examine this possibility we have filtered the catalyst **1** after the transesterification reaction of *p*-nitrophenyl acetate and allowed the filtered catalyst and the filtrate to react with another aliquot of *p*-nitrophenyl acetate, respectively, as shown in the previous study [10]. We have observed that the transesterification reaction with the filtered catalyst proceeded at the original rate, while the filtrate did show about 20% conversion within the same time interval. This result strongly suggests that the dominant reactive species is the heterogeneous catalyst **1**, not the other species such as the leached metal. However, about 20% conversion by the filtrate indicate that trace amounts of Cu metal ions might be leached during the catalysis. On the other hand, the powder X-ray diffraction (XRD) pattern of the filtered catalyst after the reaction revealed the same pattern as the original catalyst, suggesting that the original structure of the filtered catalyst has been kept during the reaction. Based on these results, we have concluded that the heterogeneous catalyst **1** could be recycled multiple times without a significant loss of activity.

The transesterification of other esters by the catalyst **1** was also carried out efficiently and the results are given in Table 1. Phenyl acetate and *p*-fluorophenyl acetate have displayed slow reactivity by the catalyst **1** (entries 2 and 3), but they were completely converted to the corresponding products, respectively. Also, the novel catalyst **1** was active to benzoates with an electron-donating or – withdrawing group that underwent the transesterification with 10 days (entries 4–6). Importantly, vinyl acetate, that is widely used as a precursor for ester synthesis, was also converted efficiently to the product methyl acetate within 2 days (entry

7), suggesting that this catalytic system can be useful for preparing various esters by transesterification. Taken all together, these results are very significant since it encourages us to construct new type of Re_6 cluster-supported catalysts that might be efficiently used as heterogeneous catalysts friendly to the environment. At this moment, however, we do not know about the exact reactive species and the reaction mechanism for the transesterification reaction by the catalyst **1**. The detailed study on these topics is ongoing.

In summary, for the first time, we synthesized hexarhenium cluster-supported $Cu_4(\mu\text{-}OH)_4$ cubanes showing a belt-like one-dimensional structure with dangling Cu_4 cubanes. Moreover, we found that the compound **1** could carry out the heterogeneous catalytic transesterification of a range of esters with methanol under the mild conditions. This catalyst system constitutes a promising class of environment-friendly heterogeneous catalysts that allowed reuse without any loss of activity through five runs with ester and appears to be an efficient, mild, and easily recyclable method for the alcoholysis of esters.

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Appendix A. Supplementary data

CCDC 293042 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.02.005.

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