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Fe_{20} Cluster Units Based Coordination Polymer from in Situ Ligand Conversion and Trapping of an Intermediate

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Supporting Information

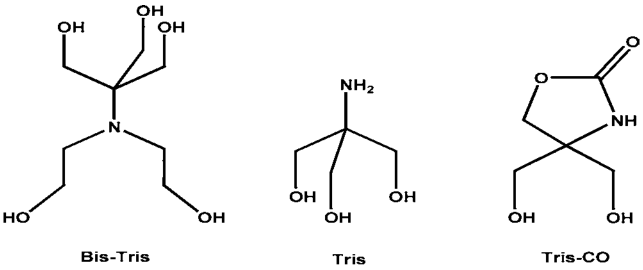
ABSTRACT: A coordination polymer based on an unprecedented Fe_{20} core has been constructed by in situ ligand conversion, including trapping of an intermediate.

The investigation of high-nuclearity metal clusters continues to be of considerable interest because they represent nice systems that span both quantum and classic phenomena.[1] To date, Ag_{490}, Mo_{368}, Fe_{168}, $La_{76}Ni_{60}$, Mn_{84}, Er_{60}, $Cu_{17}Mn_{28}$, Co_{36}, and $Fe_{16}Ln_4$ are among the largest clusters to have been studied.[2,3] Other clusters, such as Mn_{12}, Mn_{32}, Fe_4, Co_{32}, $Fe_{12}Ln_4$, $Ni_{32}La_{20}$, $Cu_{36}Ln_{24}$, and $Gd_{36}Ni_{12}$ have been also reported, and some of them show single molecule magnet (SMM) behavior.[4,5] Fe^{III} clusters are one of the largest families that has been explored, and among this family, Fe_{2-17},[6,7] Fe_{18} wheel or chain, Fe_{19} cluster,[8] Fe_{22} rod, Fe_{28} wheel, Fe_{64} cube, and Fe_{168} cage[9] are some of largest Fe^{III} clusters that are known. However, the synthesis of other large Fe^{III} clusters is still a challenging task.

Hydro/solvothermal method is an effective tool for preparing complicated coordination systems, in which in situ ligand reaction may occasionally occur.[10] Although there are drawbacks in the prediction of the final structures of crystalline products due to ligand variation, the in situ metal/ligand reaction has been extensively applied as a shortcut to obtaining novel or unexpected coordination systems.[11] So far, a variety of in situ reactions have been reported, and some typical examples have been also reviewed.[12] Unfortunately, the mechanism for such a reaction is not well understood because of the complexity of the reaction systems and the limitations of the reaction conditions, especially when the in situ reaction is not just one step. Thus, the capture of an intermediate product will not only benefit the construction of new materials with unusual architectures but also facilitate the precise clarification of their formation mechanism.[12]

Herein, an Fe^{III} coordination polymer, $\{[Fe_{20}(\mu_3\text{-}O)_{14}(Tris)_2(Tris\text{-}CO)_2(C_6H_{11}CO_2)_{24}]\cdot 2CH_3CN\}_n$ (**1**), with an icosanuclear Fe^{III} cluster as the building block, was synthesized under solvothermal conditions from the reaction of Fe^{III} precursor $[Fe_3O(C_6H_{11}CO_2)_6(H_2O)_3]\cdot C_6H_{11}CO_2$ with 2-[bis(2-hydroxyethyl)amino]-2-(hydroxymethyl)propane-1,3-diol (**Bis-Tris**; Scheme 1).[13] During this course, the starting ligand of **Bis-Tris** suffers a two-step in situ transformation (Scheme S1 in the Supporting Infomation, SI), and a cyclic ketal, namely, 4,4-bis(hydroxymethyl)oxazolidin-2-one (**Tris-CO**), seems to have been generated from the intermediate 2-amino-2-(hydroxymethyl)propane-1,3-diol (**Tris**). Notably, the intermediate of the in situ reaction was also trapped and involved in the final material.

Scheme 1. Chemical Structures of Bis-Tris, Tris, and Tris-CO



Complex **1** crystallizes in the $P2_1/c$ space group with a quite complicated asymmetric unit (Figure S1 in the SI) and consists of a 3+ oxidation state icosanuclear iron cluster (Table S1 in the SI). Single-crystal X-ray diffraction analysis indicates that the complex has a 2D (4,4) network structure (Figure 1a), where the leaflike icosanuclear Fe^{III} cores are linked by single-atom O bridges (Figure 1b). The Fe_{20}-cluster unit contains 12 six-coordinated, 6 five-coordinated, and 2 four-coordinated Fe^{III} ions, joined by 14 μ_3-O bridges, 24 cyclohexanecarboxylate ligands, and two $\mathbf{Tris}^{2-}$ and two $\mathbf{Tris\text{-}CO}^{2-}$ linkers. The length, width, and thickness of the Fe_{20} unit are 28.01, 21.78, and 19.21 Å, respectively (Figure S2 in the SI). All of the Fe−O bond lengths are in the range of 1.85−2.25 Å, and the Fe−N bond lengths are 2.18 Å. The Fe_{20} cluster can also be viewed as a Fe_{10} wheel that is centered by an open dicubane Fe_4 core to form a Fe_{14} disk and then connected by two O-centered Fe^{III} triangles via O^{2-} bridges (Figure 2).

In this case, the Fe^{III} centers exhibit three different coordination geometries: a four-coordinated quasi-tetrahedron (FeO_4), a five-coordinated slightly distorted square pyramid (FeO_5), and six-coordinated distorted octahedra (FeO_5N and FeO_6; Figure S3 in the SI). Although both $\mathbf{Tris}^{2-}$ and $\mathbf{Tris\text{-}CO}^{2-}$ act as tridentate ligands to join four Fe^{III} centers, their linking modes are different (Figure S4 in the SI). Two $\mathbf{Tris}^{2-}$ ligands connect four Fe^{III} centers to construct a Fe_4 open dicubane motif (Figure 2a), which connected the Fe_{10} wheel (Figure 2b) built by 10 O^{2-} bridges and 10 cyclohexanecarboxylate ligands to form a Fe_{14} disk (Figure 2d) through two extra O^{2-} linkers and six O^{2-} bridges in the wheel. Then, the Fe_{14} disk is further linked to two O-centered Fe^{III} triangles (Figure

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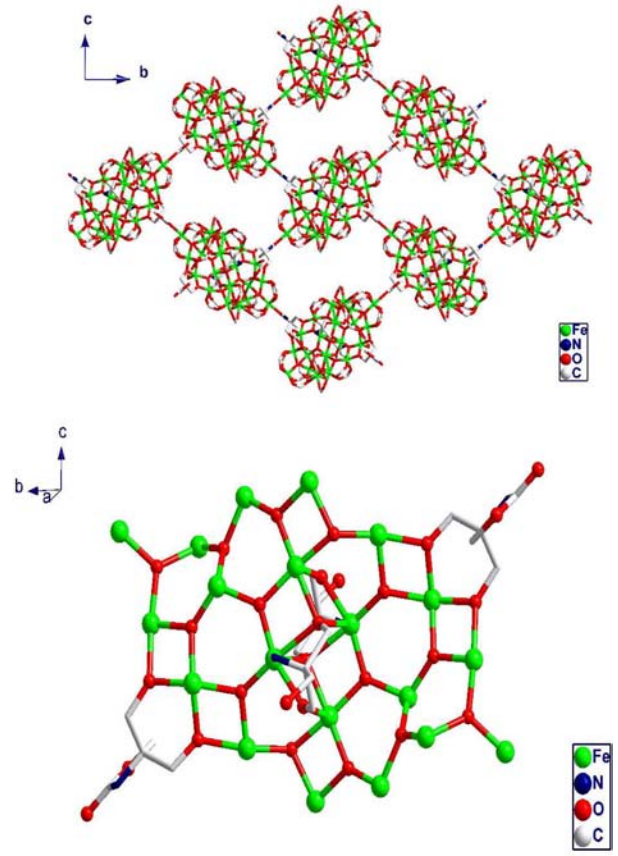

Figure 1. Structural diagrams for complex **1**: 2D (4,4) network based on Fe$_{20}$ units (top); a leaflike Fe$_{20}$ core (bottom). H atoms and cyclohexanecarboxylate ligands are omitted for clarity.

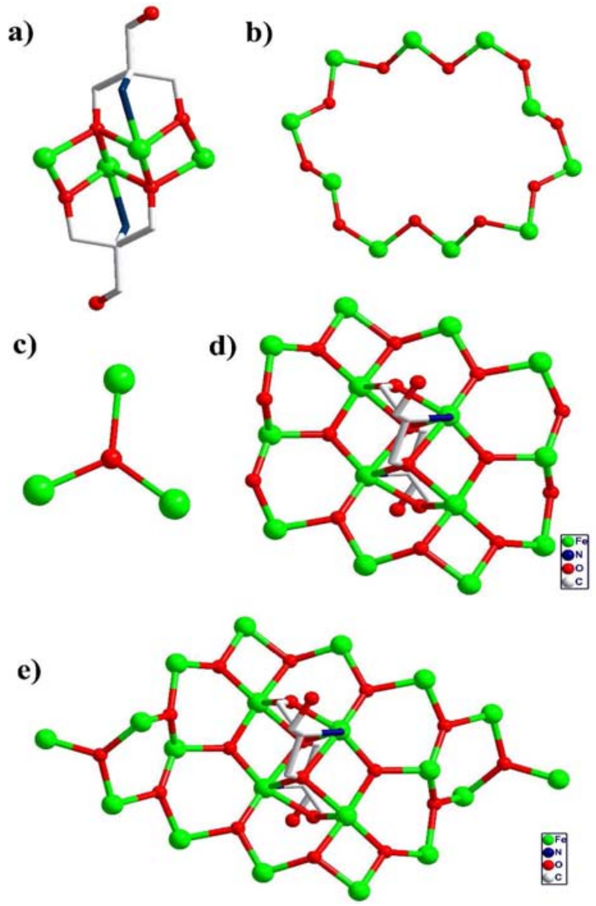

Figure 2. Subunit of the Fe$_{20}$ core in **1**: (a) Fe$_4$ core; (b) Fe$_{10}$ wheel; (c) O-centered Fe^{III} triangle; (d) Fe$_{14}$ disk; (e) leaflike Fe$_{20}$ core.

2c) to complete the leaflike Fe$_{20}$ structure via two cyclohexanecarboxylate and four O^{2-} bridges in the wheel (Figure 2e). Although large iron clusters, such as Fe$_{168}$, Fe$_{64}$, Fe$_{28}$, and Fe$_{22}$, have been documented,[2c,9] to our knowledge, this is the first example of an icosanuclear Fe^{III} cluster. Compared with the different subunits in Fe$_{28}$ and Fe$_{168}$ (Fe$_7$ units connected by a three-atom bridge) and Fe$_{64}$ (Fe$_8$ units connected by formate),[2c,9a,b] the Fe$_{20}$ units in **1** are connected by single-atom O bridges, similar to that in Fe$_{22}$ reported before.[9c] Interestingly, the 20 Fe^{III} centers in **1** are arranged in a quasi-plane pattern, which is usually observed in Fe^{III} clusters with lower nuclearity.[6b,7b] Finally, the ligand of **Tris-CO**$^{2-}$ connects three Fe^{III} centers (two from the wheel and one from the O-centered Fe^{III} triangle) in one Fe$_{20}$ unit with a Fe^{III} center from the O-centered Fe^{III} triangle in another Fe$_{20}$ core to build a 2D (4,4) network. Although coordination polymers based on Fe$_{13}$ cores have been reported,[7c] complex **1** represents the unprecedented polymeric Fe^{III} system with high-nuclearity building blocks.

In this system, **Bis-Tris** (usually as a biological buffer) with five hydroxyl groups was chosen as the starting ligand[14] to obtain high-nuclearity clusters, and two-step in situ ligand conversion may have occurred for **Bis-Tris** under solvothermal conditions (Scheme S1 in the SI). This observation is quite rare,[15] in spite of the fact that more than 10 types of hydro/solvothermal in situ ligand reactions have been known.[16] First, **Bis-Tris** might be transformed into **Tris**, which is a biochemical reagent and has been reported in metal clusters[17] due to thermal decomposition. Interestingly, a portion of **Tris** links four Fe^{III} centers in a tridentate mode and is comprised of the Fe$_4$ core in the structural assembly of **1**.[15a] Then, the intermediate **Tris** is changed to a cyclic ketal ligand, **Bis-CO**, via a cyclization reaction, which is usual for protection of the C=O group in organic synthesis. Notably, using **Tris** as the starting ligand, which can be converted into **Tris-CO** in just one step, to synthesize complex **1** was unsuccessful, revealing the critical role of **Bis-Tris** in this reaction system.

The temperature dependence of $\chi_m T$ for complex **1** as a $\chi_m T$ vs T plot (χ_m is the molar magnetic susceptibility for 20 Fe^{III} ions) in the range of 2−300 K, under an applied field of 1 kOe, is shown in Figure S9 in the SI. The $\chi_m T$ value at 300 K is 31.97 cm^3 mol^{-1} K, which is much smaller than the expected value of 87.5 cm^3 K mol^{-1} (20 isolated Fe^{III} ions with $g = 2$ and $S = {}^5/_2$) and reveals the strong antiferromagnetic interactions in the Fe$_{20}$ unit that is bridged by 14 μ_3-O^{2-} groups. This result is similar to many reported μ_3-O^{2-}-bridged Fe^{III} complexes.[5b,7c,8e,9b,18] Upon cooling, the $\chi_m T$ value decreases monotonically to 12.52 cm^3 K mol^{-1} at 6 K and then sharply to 11.57 cm^3 mol^{-1} K at 2 K, which further confirms the antiferromagnetic coupling within the Fe$_{20}$ core. The large value at 2 K implies a nonzero ground state for **1**. At 2 K, the field-dependent reduced magnetization per 20 Fe^{III} ions of **1** tends to a saturation value of 10.0 $N\beta$ at 5 T (Figure S9 in the SI), which reveals an $S = 5$ ground state for **1** that resulted from either spin frustration or some ferromagnetic interactions, in spite of some dominant antiferromagnetic couplings between Fe^{III} ions. Compared to $S = 0$ for Fe$_{64}$, Fe$_{28}$, and Fe$_{22}$[9] and an uncertain low-spin ground state for Fe$_{168}$,[2c] complex **1** is a rare example with a nonzero-spin ground state for Fe^{III} clusters with nuclearity larger than 20, in spite of $S = {}^{33}/_{2}$ for SMMs Fe$_{19}$.[8c] Alternating-current (ac) magnetic susceptibility was collected at different frequencies. $\chi'_{m}T$ is almost 14 cm^3 mol^{-1} K in the range of 15−2 K, indicating a low population of excited states in this temperature range. Extrapolation of the data from above 15 to 0 K gives about 13.5 cm^3 K mol^{-1}, confirming an $S = 5$ ground state for **1**. However, the lack of a positive signal in out-of-phase ac magnetic susceptibility precludes **1** from an SMM.

In conclusion, a 2D coordination polymer based on unprecedented Fe$_{20}$ clusters has been successfully synthesized through the two-step in situ ligand reaction, which displays a ground state of $S = 5$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic details (CIF), experimental section, supplementary structural figures, and additional characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For example, see: (a) Müller, A.; Henry, M. *C. R. Chim.* **2003**, *6*, 1201 and references cited therein. (b) Fenske, D.; Persau, C.; Dehnen, S.; Anson, C. E. *Angew. Chem., Int. Ed.* **2004**, *43*, 305. (c) Bai, J.-F.; Virovets, A. V.; Scheer, M. *Science* **2003**, *300*, 781. (d) Wernsdorfer, W.; Aliaga-Alcalde, N.; Hendrickson, D. N.; Christou, G. *Nature* **2002**, *416*, 406. (e) Bogani, L.; Wernsdorfer, W. *Nat. Mater.* **2008**, *7*, 179.

(2) (a) Anson, C. E.; Eichhöfer, A.; Issac, I.; Fenske, D.; Fuhr, O.; Sevillano, P.; Persau, C.; Stalke, D.; Zhang, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 1326. (b) Müller, A.; Beckmann, E.; Bögge, H.; Schmidtmann, M.; Dress, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1162. (c) Zhang, Z.-M.; Yao, S.; Li, Y.-G.; Clérac, R.; Lu, Y.; Su, Z.-M.; Wang, E.-B. *J. Am. Chem. Soc.* **2009**, *131*, 14600. (d) Kong, X.-J.; Long, L.-S.; Huang, R.-B.; Zheng, L.-S.; Harrisc, T. D.; Zheng, Z.-P. *Chem. Commun.* **2009**, 4354. (e) Tasiopoulos, A. J.; Vinslava, A.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 2117.

(3) (a) Kong, X.-J.; Wu, Y.-L.; Long, L.-S.; Zheng, L.-S.; Zheng, Z.-P. *J. Am. Chem. Soc.* **2009**, *131*, 6918. (b) Wang, W.-G.; Zhou, A.-J.; Zhang, W.-X.; Tong, M.-L.; Chen, X.-M.; Nakano, M.; Beedle, C. C.; Hendrickson, D. N. *J. Am. Chem. Soc.* **2007**, *129*, 1014. (c) Alborés, P.; Rentschler, E. *Angew. Chem., Int. Ed.* **2009**, *48*, 9366. (d) Baniodeh, A.; Hewitt, I. J.; Mereacre, V.; Lan, Y.-H.; Novitchi, G.; Anson, C. E.; Powell, A. K. *Dalton Trans.* **2011**, *40*, 4080.

(4) (a) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141. (b) Manoli, M.; Inglis, R.; Manos, M. J.; Nastopoulos, V.; Wernsdorfer, W.; Brechin, E. K.; Tasiopoulos, A. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 4441. (c) Barra, A. L.; Caneschi, A.; Cornia, A.; De Biani, F. F.; Gatteschi, D.; Sangregorio, C.; Sessoli, R.; Sorace, L. *J. Am. Chem. Soc.* **1999**, *121*, 5302.

(5) (a) Bi, Y. F.; Wang, X. T.; Liao, W. P.; Wang, X. F.; Wang, X. W.; Zhang, H. J.; Gao, S. *J. Am. Chem. Soc.* **2009**, *131*, 11650. (b) Zeng, Y.-F.; Xu, G.-C.; Hu, X.; Chen, Z.; Bu, X.-H.; Gao, S.; Sañudo, E. C. *Inorg. Chem.* **2010**, *49*, 9734. (c) Kong, X.-J.; Ren, Y.-P.; Long, L.-S.; Zheng, Z.-P.; Huang, R.-B.; Zheng, L.-S. *J. Am. Chem. Soc.* **2007**, *129*, 7016. (d) Leng, J.-D.; Liu, J.-L.; Tong, M.-L. *Chem. Commun.* **2012**, *48*, 5286. (e) Peng, J.-B.; Zhang, Q.-C.; Kong, X.-J.; Ren, Y.-P.; Long, L.-S.; Huang, R.-B.; Zheng, L.-S.; Zheng, Z. *Angew. Chem., Int. Ed.* **2011**, *50*, 10649.

(6) (a) Miao, Y.-L.; Liu, J.-L.; Lin, Z.-J.; Ou, Y.-C.; Leng, J.-D.; Tong, M.-L. *Dalton Trans.* **2010**, *39*, 4893. (b) Oshio, H.; Hoshino, N.; Ito, T.; Nakano, M.; Renz, F.; Gülich, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 223. (c) Graham, K.; Ferguson, A.; Douglas, F. J.; Thomas, L. H.; Murrie, M. *Dalton Trans.* **2011**, *40*, 3125. (d) Stamatatos, T. C.; Christou, A. G.; Jones, C. M.; O'Callaghan, B. J.; Abboud, K. A.; O'Brien, T. A.; Christou, G. *J. Am. Chem. Soc.* **2007**, *129*, 9840.

(7) (a) Gorun, S. M.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 3337. (b) Raptopoulou, C. P.; Tangoulis, V.; Devlin, E. *Angew. Chem., Int. Ed.* **2002**, *41*, 2386. (c) Murugesu, M.; Clérac, R.; Wernsdorfer, W.; Anson, C. E.; Powell, A. K. *Angew. Chem., Int. Ed.* **2005**, *44*, 6678. (d) Micklitz, W.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 6856.

(8) (a) Goodwin, J. C.; Sessoli, R.; Gatteschi, D.; Wernsdorfer, W.; Powell, A. K.; Heath, S. L. *Dalton Trans.* **2000**, 1835. (b) Powell, A. K.; Heath, S. L.; Gatteschi, D.; Pardi, L.; Sessoli, R.; Spina, G.; Del Giallo, F.; Pieralli, F. *J. Am. Chem. Soc.* **1995**, *117*, 2491. (c) King, P.; Stamatatos, T. C.; Abboud, K. A.; Christou, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 7379. (d) Watton, S. P.; Fuhrmann, P.; Pence, L. E.; Caneschi, A.; Cornia, A.; Abbati, G. L.; Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2774. (e) Taguchi, T.; Thompson, M. S.; Abboud, K. A.; Christou, G. *Dalton Trans.* **2010**, *39*, 9131. (f) Bagai, R.; Abboud, K. A.; Christou, G. *Chem. Commun.* **2007**, 3359.

(9) (a) Liu, T.; Zhang, Y.-J.; Wang, Z.-M.; Gao, S. *J. Am. Chem. Soc.* **2008**, *130*, 10500. (b) Zhang, Z.-M.; Li, Y.-G.; Yao, S.; Wang, E.-B.; Clérac, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 1581. (c) Foguet-Albiol, D.; Abboud, K. A.; Christou, G. *Chem. Commun.* **2005**, 4282.

(10) (a) Xiong, R.-G.; Xue, X.; Zhao, H.; You, X.-Z.; Abrahams, B. F.; Xue, Z. *Angew. Chem., Int. Ed.* **2002**, *41*, 3800 and references cited therein. (b) Zhang, X.-M.; Tong, M.-L.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1029. (c) Liu, C.-M.; Gao, S.; Kou, H.-Z. *Chem. Commun.* **2001**, 1670.

(11) (a) Blake, J.; Champness, N. R.; Chung, S. S. M.; Li, W.-S.; Schröder, M. *Chem. Commun.* **1997**, 1675. (b) Han, L.; Bu, X.; Zhang, Q.; Feng, P. *Inorg. Chem.* **2006**, *45*, 5736. (c) Yang, F.-L.; Tao, J.; Huang, R.-B.; Zheng, L.-S. *Inorg. Chem.* **2011**, *50*, 911.

(12) (a) Chen, X.-M.; Tong, M.-L. *Acc. Chem. Res.* **2007**, *40*, 162. (b) Zhao, H.; Qu, Z.-R.; Ye, H.-Y.; Xiong, R.-G. *Chem. Soc. Rev.* **2008**, *37*, 84. (c) Zhang, X.-M. *Coord. Chem. Rev.* **2005**, *249*, 1201. (d) Zhu, H.-B.; Gou, S.-H. *Coord. Chem. Rev.* **2011**, *255*, 318.

(13) Weinland, R. F.; Herz, A. *Ber. Deutsch. Chem. Ges.* **1912**, *45*, 2662.

(14) (a) Ferguson, A.; Parkin, A.; Murrie, M. *Dalton Trans.* **2006**, 3627. (b) Ferguson, A.; McGregor, J.; Parkin, A.; Murrie, M. *Dalton Trans.* **2008**, 731. (c) Stamatatos, T. C.; Abboud, K. A.; Christou, G. *Dalton Trans.* **2009**, 41.

(15) (a) Li, G.-B.; Liu, J.-M.; Yu, Z.-Q.; Wang, W.; Su, C.-Y. *Inorg. Chem.* **2009**, *48*, 8659. (b) Mothe, S. R.; Kothandaraman, P.; Rao, W.; Chan, P. W. H. *J. Org. Chem.* **2011**, *76*, 2521. (c) Wang, Q.-F.; Song, X.-K.; Chen, J.; Yan, C.-G. *J. Comb. Chem.* **2009**, *11*, 1007.

(16) Kong, X.-J.; Zhuang, G.-L.; Ren, Y.-P.; Long, L.-S.; Huang, R.-B.; Zheng, L.-S. *Dalton Trans.* **2009**, 1707 and references cited therein.

(17) (a) Ferguson, A.; Parkin, A.; Sanchez-Benitez, J.; Kamenev, K. V.; Wernsdorfer, W.; Murrie, M. *Chem. Commun.* **2007**, *33*, 3473. (b) Mondal, K. C.; Song, Y.; Mukherjee, P. S. *Inorg. Chem.* **2007**, *46*, 9736.

(18) Hoshino, N.; Ako, A. M.; Powell, A. K.; Oshio, H. *Inorg. Chem.* **2007**, *48*, 3396.