A Single-Bridge Strategy for Synthesis of a 3-D Heterobimetallic Cluster with a Heavily Distorted Diamondoid Topology and Enhanced Third-Order Nonlinear Optical Properties

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ABSTRACT: A novel three-dimensional heterobimetallic cluster $\{[Bu_4N][WS_4Cu_3(CN)_2]\}_n$ (**1**) with a heavily distorted diamondoid topology was constructed from the T-shaped building clusters $[WS_4Cu_3]^+$ and single cyanide bridges in a 4-connected mode; this cluster shows strong third-order nonlinear optical properties.

The design and synthesis of multidimensional coordination compounds have continued to attract considerable interest for both the intriguing architectures and the physical properties of the resultant materials.[1] M/S/Cu (M = Mo, W) clusters have long been explored for their diverse coordination modes and potential applications, particularly in third-order nonlinear optical (NLO) materials.[2–4] Although a rich variety of ligands and building units have been used to synthesize M/S/Cu clusters,[2,4] crystal engineering of multidimensional clusters with well-defined geometries still faces great challenges to control the complexity and diversity of the frameworks.[4] It is noteworthy that multidimensional M/S/Cu cluster frameworks are usually constructed from double-bridging ligands, which has limited both the fabrication of such polymeric clusters and the diversity of cluster architecture;[4–9] to the best of our knowledge, except for "planar" open clusters $[MS_4Cu_4]^{2+}$ and the nest-shaped cluster $[WOS_3Cu_3]^+$,[6–9] no three-dimensional (3-D) M/S/Cu clusters have thus far been constructed using other building units. In contrast to double-bridging ligands, single bridges can play a unique role in the construction of multidimensional M/S/Cu clusters; for example, the first two-dimensional (2-D) W/S/Cu cluster, constructed from the linear building clusters $[WS_4Cu_2]$, is connected by single cyanide bridges.[5b] These aforementioned investigations inspired us to explore a single-bridge strategy for the generation of novel 3-D M/S/Cu clusters, employing building clusters other than $[MS_4Cu_4]^{2+}$ and $[WOS_3Cu_3]^+$. We report herein a novel 3-D cluster $\{[Bu_4N][WS_4Cu_3(CN)_2]\}_n$ (**1**) with a heavily distorted diamondoid network, which is linked through single cyanide bridges only, the first 3-D example of Mo(W)/S/Cu clusters constructed by the 4-connected T-shaped building clusters $[WS_4Cu_3]^+$. Z-scan studies of **1** reveal strong third-order NLO properties.

The reaction of $(NH_4)_2WS_4$ and CuBr (molar ratio of 1:3) in dimethylformamide (DMF) led to an orange-red solution. After stirring and filtration and then layering the filtrate with a solution of $(Bu_4N)CN$ in *i*-PrOH for several days, **1** was obtained as orange-red block crystals (yield: 36% based on W).[10] X-ray crystallographic analysis revealed that **1** crystallizes in the tetragonal chiral space group $P4_32_12$,[11] and each $[WS_4Cu_3]^+$ in **1** is linked by another four $[WS_4Cu_3]^+$ units through single cyanide bridges to furnish a novel 3-D framework (Figure 1).

As shown in Figure 2a, the building cluster $[WS_4Cu_3]^+$ with a 4-connected mode exhibits C_2 symmetry. Cu2−W1−Cu2a and Cu2−W1−Cu1 angles are 177.67(13)° and 88.83(6)°, respectively, giving rise to a nearly T-shaped arrangement for each building cluster $[WS_4Cu_3]^+$. In each $[WS_4Cu_3]^+$, three Cu atoms have two kinds of coordination environments; one is coordinated by two μ_3-S and two cyanide bridges, forming a tetrahedral geometry, and another two have a triangular coordination geometry formed by one μ_2-S, one μ_3-S atom, and one cyanide bridge. The W atom possesses a tetrahedral coordination geometry through bonding to two μ_2-S and two μ_3-S atoms, with the S−W−S angles ranging from 107.5(2) to 111.1(2)°. The bond lengths of Cu−μ_2-S (Cu2−S1, 2.230(7) Å) are comparable to those of Cu−μ_3-S (Cu2−S2, 2.235(6) Å; Cu1−S2, 2.333(5) Å), while bond lengths of W−μ_2-S (W1−S1, 2.187(5) Å) are shorter than those of W−μ_3-S (W1−S2, 2.234(4) Å), which leads to the expected shortening of the W1···Cu2 distance (2.650(2) Å) in comparison with the W1···Cu1 distance (2.740(3) Å).

Network analysis of **1** reveals that the short vertex symbol of **1** is 6^6, the same as those of 3-D M/S/Cu clusters with diamondoid topological networks that were constructed from $[MS_4Cu_4]^{2+}$ and $[WOS_3Cu_3]^+$.[6,8,9] Because of the T-shaped arrangement of each building cluster $[WS_4Cu_3]^+$, **1** shows an irregular 3-D 4-connected network (Figure 2b). All 6-membered rings possess highly distorted chair forms,[12] which results in a heavily distorted diamondoid topological network for **1**.

The packing diagram in Figure 1 exhibits two kinds of irregular shaped channels, while both the building clusters and channels show an unusual ABCD stacking manner. One-dimensional (1-D) square-like channels can be seen down the *c*-axis (Figure 3a), while viewed along the *a*- or *b*-axis, the packing diagram of **1** reveals 1-D peanut-shaped channels (Figure 3b). Interestingly, examining the [100], [010], and [001] planes of **1** (Figure 3) shows that the channels in every two adjacent layers adopt different stacking behavior, in contrast to adjacent channels in the [111] plane which stack in the same manner (Figure S2, Supporting Information).

T-shaped building clusters $[MS_4Cu_3]^+$ (M = Mo, W) have been used previously to construct polymeric M/S/Cu clusters (for example, $\{[Et_4N]_2[WS_4Cu_3(SCN)_3]\}_n$ **a**[13] and $\{[PPh_4][WS_4Cu_3-(CN)_2]\cdot MeCN\}_n$ **b**[5b]). However, each $[WS_4Cu_3]^+$ in **a** is linked through double bridges that form an infinite 1-D chain, while the building clusters in **b** are connected by both single and double bridges, resulting in an infinite 2-D network. In the present study, the same building clusters as those in **a** and **b** are assembled to construct the new 3-D framework of **1** via single bridges only. In particular, **b** possesses the same anionic composition as **1**, but has a 2-D rather than a 3-D structure because of the presence of some

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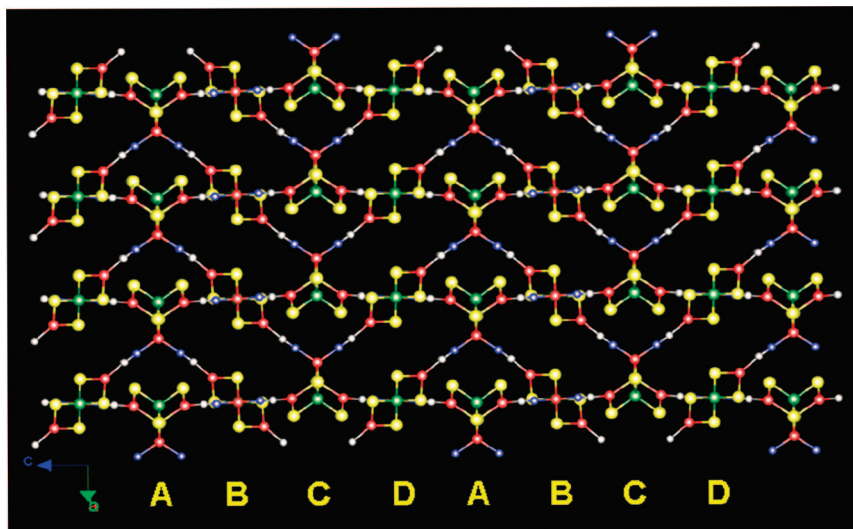‡ Suzhou University.
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Figure 1. Packing diagram of **1** (ball-and-stick representation), showing each T-shaped building cluster in a 4-connected topology and channels in an ABCD stacking manner (cations of **1** are omitted for clarity; S yellow, C grey, N blue, Cu red, W green).
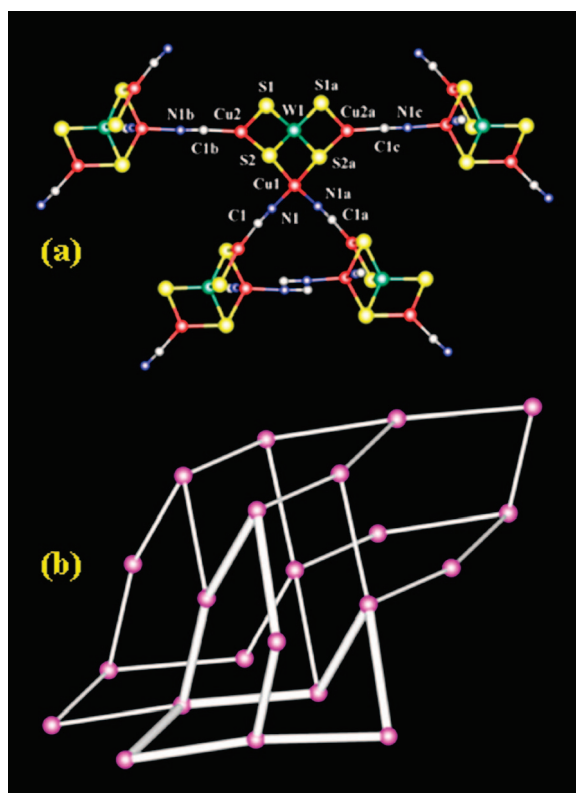

Figure 2. (a) Partial view of the 3-D anionic ball-and-stick plot for **1**, showing the 4-connected mode of the T-shaped building cluster $[WS_4Cu_3]^+$ (S yellow, C grey, N blue, Cu red, W green); (b) a fragment of the heavily distorted diamondoid network emphasizing two six-membered rings; the pink balls and white sticks represent the T-shaped building clusters $[WS_4Cu_3]^+$ and single cyanide bridges, respectively.
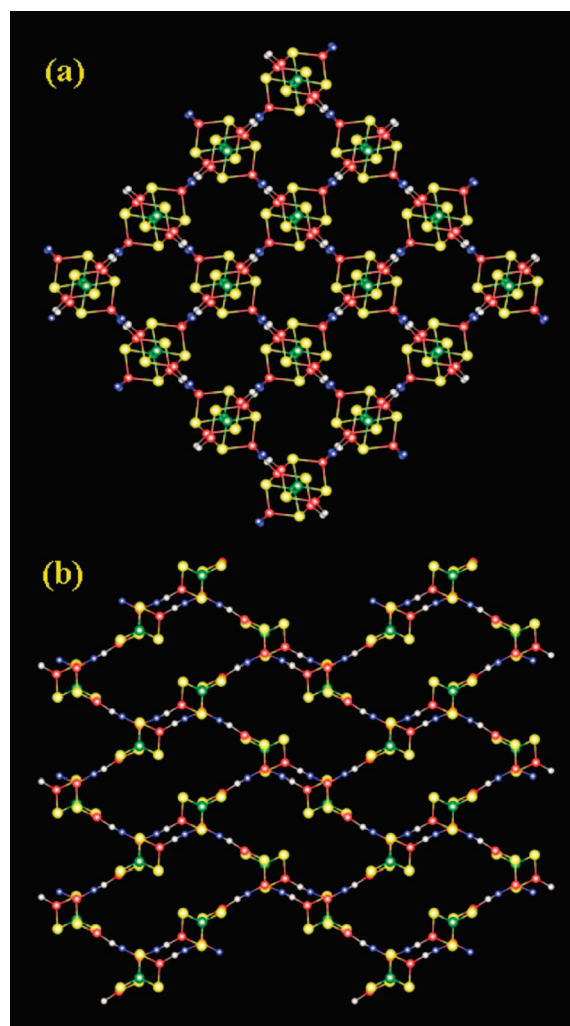

Figure 3. Packing diagram of **1** (ball-and-stick representation), viewed along (a) the *c*-axis and (b) the *a*- or *b*-axis, showing the interlaced square-like and peanut-shaped channels, respectively (cations of **1** are omitted for clarity; S yellow, C grey, N blue, Cu red, W green).

double bridges. The single-bridging ligands clearly play a crucial role in the generation of the 3-D framework of **1**. Clusters with larger connectivity numbers afford more complex and diverse frameworks; for example, M/S/Cu clusters with a 3-connected mode tend to form 2-D network structures,[5b] while clusters in a 4-connected mode usually form 3-D frameworks.[6–9] From a topological perspective, building units of multidimensional M/S/Cu clusters will have larger connectivity numbers when linked in

a single-bridge manner than the same building units linked in a double-bridge manner. Thus, **1** possesses a 3-D framework because
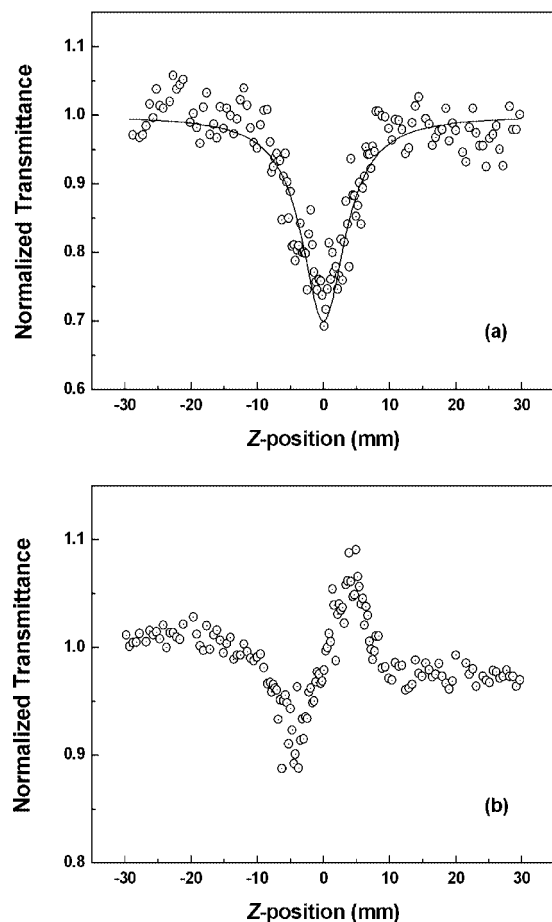
Figure 4. Z-scan measurement of **1** in 5.33×10^{-4} mol dm^{-3} DMF solution at 532 nm: (a) data collected under the open-aperture configuration; (b) data obtained by dividing the normalized Z-scan data obtained under the closed-aperture configuration by the normalized Z-scan data in (a).

of its T-shaped building clusters in a 4-connected mode, which benefits from the single-cyanide-bridge connection; this differs from **a** and **b**, which have 1-D and 2-D frameworks for their 2- and 3-connected modes, respectively. This may imply that a single-bridge strategy using building clusters other than $[MS_4Cu_4]^{2+}$ and $[WOS_3Cu_3]^+$ should be effective for the construction of new 3-D M/S/Cu clusters with a variety of intriguing geometries.

The third-order NLO absorptive and refractive properties of **1** were measured by the Z-scan method[14] with linearly polarized 4.5-ns pulses at 532 nm generated from a Q-switched frequency-doubled Nd:YAG laser, showing that **1** has strong effective third-order NLO absorptive and refractive properties, as illustrated in Figure 4. The nonlinear absorption component was evaluated under an open-aperture configuration, and the nonlinear refractive property was assessed by dividing the normalized Z-scan data obtained under the closed-aperture configuration by the normalized Z-scan data obtained under the open-aperture configuration. The valley/peak pattern of the corrected transmittance curve shows that **1** exhibits self-focusing behavior. The NLO absorptive coefficient α_2 of **1** was calculated to be $(7.5 \pm 0.6) \times 10^{-11}$ m W^{-1}. With the measured value of the difference in the normalized transmittance values at the valley and peak positions, the NLO refractive index n_2 was calculated to be $(1.2 \pm 0.1) \times 10^{-11}$ esu. In accordance with the observed α_2 and n_2 values, the modulus of the effective third-order susceptibility $\chi^{(3)}$ was calculated to be $(3.6 \pm 0.3) \times 10^{-12}$ esu; the corresponding modulus of the hyperpolarizability γ of $(3.4 \pm 0.3) \times 10^{-30}$ esu was obtained from $\chi^{(3)} = \gamma NF^4$, where N is the number density (concentration) of cluster in the sample solution and $F^4 = 3.3$ is the local field correction factor. The hyperpolar-

izability γ of **1** is larger than those of many other heterobimetallic chalcogenide clusters with different cluster skeletons (for representative examples, see Table S1, Supporting Information[15]), which indicates that **1** will be a promising candidate for NLO materials.

In conclusion, by exploiting single-cyanide bridges and T-shaped building clusters, we have successfully constructed a novel 3-D W/S/Cu cluster with a heavily distorted diamondoid topology. In contrast to double bridges, single bridges can link the same building clusters to form more complex and diverse frameworks. Further studies of the formation of new multidimensional heterobimetallic clusters constructed by various single bridges and building clusters are currently in progress.

Supporting Information Available: Experimental section; optical and other characterization measurements and preparation; Figure S1, Figure S2, and Table S1; X-ray crystallographic file in CIF format for **1**. This information is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Wang, Z. Q.; Kravtsov, V. C.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 2877. (b) Huang, X. C.; Lin, Y. Y.; Zhang, J. P.; Chen, X. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1557. (c) Eddaoudi, M.; Moler, D. B.; Li, H. L.; Chen, B. L.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (d) Evans, O. R.; Lin, W. B. *Acc. Chem. Res.* **2002**, *35*, 511. (e) Oh, M.; Carpenter, G. B.; Sweigart, D. A. *Acc. Chem. Res.* **2004**, *37*, 1.

(2) (a) Zhang, C.; Jin, G. C.; Chen, J. X.; Xin, X. Q.; Qian, K. P. *Coord. Chem. Rev.* **2001**, *213*, 51. (b) Hou, H. W.; Xin, X. Q.; Shi, S. *Coord. Chem. Rev.* **1996**, *153*, 25.

(3) (a) Zhang, C.; Song, Y. L.; Wang, X. *Coord. Chem. Rev.* **2007**, *251*, 111. (b) Müller, A.; Diemann, E.; Jostes, R.; Bogge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934. (c) Lee, S. C.; Holm, R. H. *Chem. Rev.* **2004**, *104*, 1135. (d) Shi, S.; Ji, W.; Tang, S. H.; Lang, J. P.; Xin, X. Q. *J. Am. Chem. Soc.* **1994**, *116*, 3615. (e) Zhang, C.; Song, Y. L.; Kühn, F. E.; Wang, Y. X.; Xin, X. Q.; Herrmann, W. A. *Adv. Mater.* **2002**, *14*, 818. (f) Zhang, C.; Song, Y. L.; Fung, B. M.; Xue, Z. L.; Xin, X. Q. *Chem. Commun.* **2001**, 843.

(4) Niu, Y. Y.; Zheng, H. G.; Hou, H. W.; Xin, X. Q. *Coord. Chem. Rev.* **2004**, *248*, 169.

(5) (a) Lang, J. P.; Xu, Q. F.; Zhang, W. H.; Li, H. X.; Ren, Z. G.; Chen, J. X.; Zhang, Y. *Inorg. Chem.* **2006**, *45*, 10487. (b) Lang, J. P.; Jiao, C. M.; Qiao, S. B.; Zhang, W. H.; Abrahams, B. F. *Inorg. Chem.* **2005**, *44*, 3664.

(6) (a) Liang, K.; Zheng, H. G.; Song, Y. L.; Lappert, M. F.; Li, Y. Z.; Xin, X. Q.; Huang, Z. X.; Chen, J. T.; Lu, S. F. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 5776. (b) Huang, K. X.; Song, Y. L.; Pan, Z. R.; Li, Y. Z.; Zhuo, X.; Zheng, H. G. *Inorg. Chem.* **2007**, *46*, 6233.

(7) Manoli, J. M.; Potvin, C.; Sécheresse, F.; Marzak, S. *Chem. Commun.* **1986**, 1557.

(8) Zhang, C.; Song, Y. L.; Xu, Y.; Fun, H. K.; Fang, G. Y.; Wang, Y. X.; Xin, X. Q. *J. Chem. Soc., Dalton Trans.* **2000**, 2823.

(9) Lang, J. P.; Xu, Q. F.; Yuan, R. X.; Abrahams, B. F. *Angew. Chem., Int. Ed.* **2004**, *43*, 4741.

(10) Characterization for **1**: Anal. Calcd. for $C_{18}H_{36}Cu_3N_3S_4W$ (%): C, 27.12; H, 4.55; N, 5.27. Found C, 27.15; H, 4.57; N, 5.25. IR data (KBr pellets, cm^{-1}): 2151(vs), 1477(s), 1378(s), 882(s), 738(s), 464(vs), 436(vs).

(11) Crystallographic data for $C_{18}H_{36}Cu_3N_3S_4W$ **1**: $M = 797.27$, tetragonal, space group $P4_32_12$, $a = 10.9115(15)$, $b = 10.9115(15)$, $c = 23.638(5)$ Å, $V = 2814.4(8)$ Å^3, $Z = 4$, $T = 293(2)$ K, $D_c = 1.882$ g cm^{-3}, μ(Mo-Kα) = 6.617 mm^{-1}, 3112 reflections measured, 2758 unique [$R_{(int)} = 0.0707$] which were used in the calculations. The final $R_1 = 0.0641$, $wR_2 = 0.1220$ for 1682 reflections with $I > 2\sigma(I)$ and 134 variable parameters, $S = 1.026$. Largest diffraction peak/hole is $1.154/-0.881$ e Å^{-3}. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques.

(12) (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (b) O'Keeffe, M.; Eddaoudi, M.; Li, H. L.; Reineke, T.; Yaghi, O. M. *J.*

Solid State Chem. **2000**, *152*, 3. (c) Bi, M. H.; Li, G. H.; Zou, Y. C.; Shi, Z.; Feng, S. H. *Inorg. Chem.* **2007**, *46*, 604.

(13) Manoli, J. M.; Potvin, C.; Sécheresse, F.; Marzak, S. *Inorg. Chim. Acta* **1988**, *150*, 257.

(14) Sheik-Bahae, M.; Said, A. A.; Wei, T. H.; Hagan, D. J.; van Stryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760.

(15) (a) Zhang, W. H.; Chen, J. X.; Li, H. X.; Wu, B.; Tang, X. Y.; Ren, Z. G.; Zhang, Y.; Lang, J. P.; Sun, Z. R. *J. Organomet. Chem.* **2005**, *690*, 394. (b) Zhang, C.; Song, Y. L.; Jin, G. C.; Fang, G. Y.; Wang, Y. X.; Raj, S. S. S.; Fun, H. K.; Xin, X. Q. *J. Chem. Soc., Dalton Trans.* **2000**, 1317. (c) Zhang, C.; Song, Y. L.; Kühn, F. E.; Xu, Y.;

Xin, X. Q.; Fun, H. K.; Herrmann, W. A. *Eur. J. Inorg. Chem.* **2002**, 55. (d) Zhang, C.; Song, Y. L.; Wang, X.; Kühn, F. E.; Wang, Y. X.; Xu, Y.; Xin, X. Q. *J. Mater. Chem.* **2003**, *13*, 571. (e) Cai, Y.; Song, Y. L.; Zheng, H. G.; Niu, Y. Y.; Du, C. X.; Xin, X. Q. *Chem. Lett.* **2002**, 508. (f) Zheng, H. G.; Leung, W. H.; Tan, W. L.; Long, D. L.; Ji, W.; Chen, J. T.; Xin, F. B.; Xin, X. Q. *J. Chem. Soc., Dalton Trans.* **2000**, 2145. (g) Niu, Y. Y.; Song, Y. L.; Zheng, H. G.; Long, D. L.; Fun, H. K.; Xin, X. Q. *New J. Chem.* **2001**, *25*, 945.