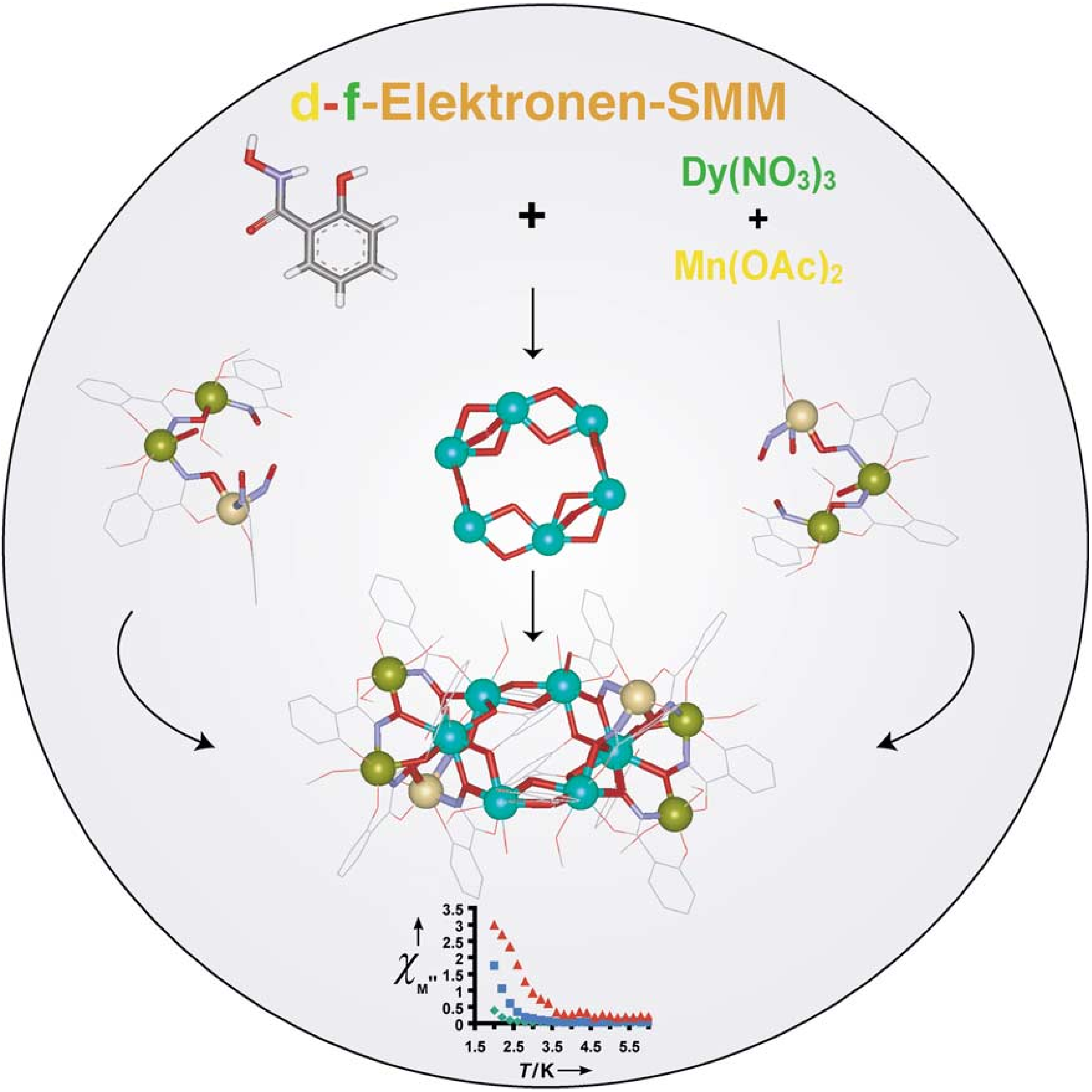
Zuschriften



Der abgebildete Dy-Mn-Cluster ist der erste, der sich wie ein Einzelmolekülmagnet verhält. Die trimeren $Mn^{III}_2Mn^{IV}$-„Flügel“ und der hexagonale Dysprosiumring bilden einen Cluster, der bei Wechselstrom-SQUID-Experimenten ein Out-of-Phase-Signal der magnetischen Suszeptibilität liefert. Einzelheiten hierzu finden Sie in der Zuschrift von M. L. Kirk, V. L. Pecoraro et al. auf den folgenden Seiten.

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Single-Molecule Magnets

Synthesis, Structure, and Magnetic Properties of a Large Lanthanide–Transition-Metal Single-Molecule Magnet**

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The chemistry of large lanthanide clusters has long been a focus of coordination chemists due to the unique properties conferred upon molecules that have f electrons. Recently, large cluster and ring compounds have been prepared with the goal of controlling the synthesis of lanthanide clusters, creating magnetic resonance imaging (MRI) contrast agents and luminescent sensors, and understanding the magnetic exchange interactions between lanthanide ions.[1] However, most of this research has been directed solely towards lanthanide clusters and not hybrid lanthanide–transition-metal clusters. Lanthanide–transition-metal cluster chemistry has primarily focused on Gd^{III}–Cu^{II} cluster systems, most notably by Kahn and co-workers, in the hope of understanding the magnetic interactions between the two different metal ions.[2a] Although subsequent work has firmly established that the Gd^{III} and Cu^{II} ions are ferromagnetically exchange coupled in the cluster,[2] few examples of lanthanide clusters with other transition metals have been realized and these tend to be small in size.[3] Recently, a $\{Cu_2Tb_2\}$ complex was reported that exhibits an out-of-phase ac magnetic susceptibility component that is consistent with it being a single-molecule magnet (SMM).[4] Previous work performed by our group has focused on the class of metallamacrocycles known as metallacrowns[5] which have interesting magnetic properties as they combine numerous metal ions in close proximity. [2d,6] Recently, we decided to return to one of the original metallacrown ligands to synthesize large complexes that contain both paramagnetic lanthanide ions and manganese ions.[5] We believed that such complexes could yield complex and interesting magnetic properties due to the large single-ion anisotropy inherent to these ions. Herein we report the largest lanthanide–manganese cluster synthesized to date, $[Dy_6Mn_6(H_2shi)_4(Hshi)_2(shi)_{10}(CH_3OH)_{10}(H_2O)_2]\cdot 9\,CH_3OH\cdot 8\,H_2O$ (H_3shi = salicylhydroxamic acid) **1**, and only the second example of a lanthanide–transition-metal complex that behaves as an SMM.[7]

The structure of **1** (Figure 1) is centered about a nearly planar hexagonal ring of Dy^{III} ions that is capped on either end by a $Mn^{III}{}_2Mn^{IV}$ trimer. The three pairs of symmetry equivalent Dy^{III} ions are interlinked by one- or two-atom bridges (Figure 2), and the Dy^{III} ions are also connected to the manganese ions by one or two-atom bridges. Dy1 and Dy2 are eight coordinate while Dy3 is nine coordinate. In addition, to two solvent oxygen atoms, Dy1 is coordinated by six ligand-derived oxygen atoms. Of particular note are two μ_2-hydroxylimino oxygen atoms that form a bridge to Dy2 (3.88 Å), and the one μ_2-phenolato oxygen atom that bridges with another μ_2-hydroxylimino oxygen atom to Dy3A (3.94 Å). Other μ_2-hydroxylimino oxygen atoms bridge Dy1 to Dy2. Remarkably, eight of the nine ligands to Dy3A form either one- or two-atom bridges to Dy or Mn atoms. The oxime that links Dy1 and Dy3A also serves to couple Dy1 and Dy3A to Mn1 (an Mn^{IV} ion) through a Dy-O-N-Mn connectivity pattern. Dy3A, which has only oxygen donors from ligands, exhibits three single-atom bridges (two from oxime oxygen atoms and one from a carbonyl oxygen atom) to Dy2A (Dy2A−Dy3A = 3.68 Å). The Dy2A ion is bound by seven ligand derived oxygen atoms and one solvent oxygen atom. Dy3A also forms either one- or two-atom bridges to all three Mn atoms (Dy3A to: Mn1, 3.70 Å; Mn2, 3.84 Å; Mn3, 3.95 Å). The Dy2A forms two atom oxime bridges to Mn1 and Mn3 (Dy2A to: Mn1, 5.01 Å; Mn3, 5.00 Å). The three Mn ions are all six coordinate with average Mn−(O,N) bond lengths of 1.91 Å for Mn1 and 2.04 Å and 2.05 Å for Mn2 and Mn3, respectively. The longer average bond lengths and the obvious Jahn–Teller axes support assignment of Mn2 and Mn3 as Mn^{III} ions. The Mn2 has a two-atom oxime bridge to Mn1 and an identical bridge to Mn3. There is no direct interaction between Mn1 and Mn3. The Mn separations are Mn1–Mn2, 4.75 Å; Mn1–Mn3, 5.98 Å and Mn2–Mn3, 4.68 Å. The three Mn ions are interconnected through the shi^{3-} ligand in a manner that is similar, but not identical, to that previously described.[5]

Due to the magnetic interactions that should arise as a result of the multiple short distances between the metal ions in the cluster, dc magnetic-susceptibility measurements were performed on a powdered sample mulled in eicosane. These data were collected on a Quantum Design dc superconducting quantum interference device (SQUID) magnetometer in the 5–300 K temperature range. The χT value decreases from 105 $cm^3\,K\,mol^{-1}$ at 300 K to 47.4 $cm^3\,K\,mol^{-1}$ at 2 K (see Supporting Information), which is indicative of dominant intramolecular antiferromagnetic exchange interactions in the cluster, depopulation of dysprosium single-ion sublevels, or a combination of both. Variable-temperature, variable-field magnetization measurements were collected on a Quantum Design physical properties measurement system

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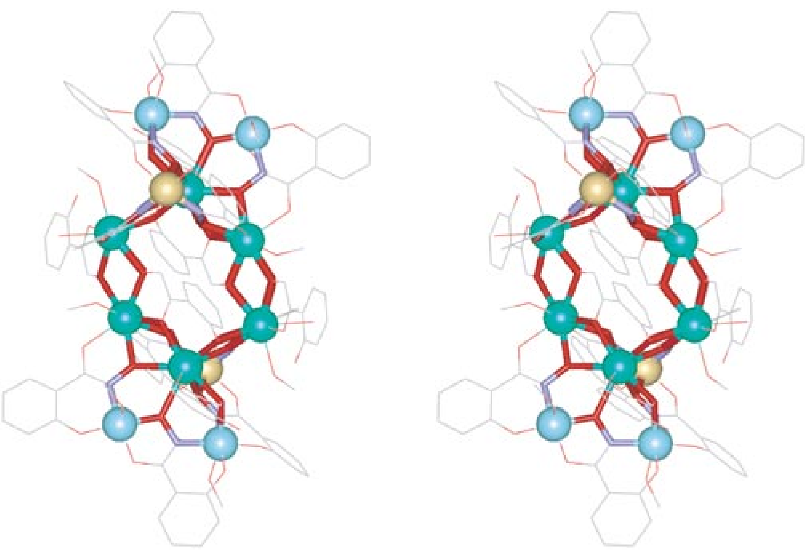

Figure 1. X-ray crystal structure of **1**. Color scheme: Green spheres Dy^{III}; blue spheres Mn^{III}; gold spheres Mn^{IV}.

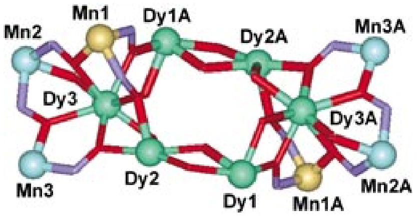

Figure 2. Highlight of one- and two-atom bridging motifs in **1**. Color scheme: See Figure 1.

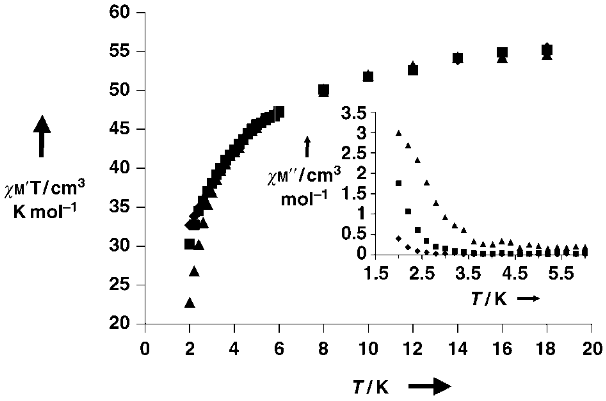

Figure 3. In-phase magnetic susceptibility of **1**. Inset: Out-of-phase magnetic susceptibility of **1**. (◆ 10 Hz; ■ 100 Hz; ▲ 1000 Hz).

(PPMS) at five different temperatures (2 K, 2.5 K, 3.33 K, 5 K, and 10 K) over an applied field range of 0.5–14 T (see Supporting Information). The magnetization values slightly decrease at low fields (<9 T) upon increasing the temperature from 2 K to 5 K, followed by a large drop in the magnitude of the magnetization at 10 K. At higher fields (>9 T) the magnetization increase linearly with the applied field and the magnetization data converge for all temperatures. The magnetization values never saturate at high fields, which indicates that either an energetically isolated spin state is never achieved even at the highest fields due to field induced level crossings and a high density of states, or there is a sizable temperature independent paramagnetism. The latter results from field-induced mixing of specific excited spin states with the ground spin state. Regardless of the reason for the observed magnetization behavior, the ground spin state for **1** can not be determined at this time.

As **1** had such a high χT value at low temperatures and contained a large number of anisotropic paramagnetic metal ions, we viewed **1** as a potential member of the relatively new SMM subclass that comprises lanthanide ion complexes.[4,8,9] Variable-temperature powder ac SQUID measurements were performed on a Quantum Design instrument from 2–100 K at frequencies of 10 Hz, 100 Hz, and 1000 Hz with a 3.5 G oscillating ac magnetic field and no applied dc magnetic field. Near 4.0 K the in-phase ac susceptibility ($\chi' T$) signal begins to decrease and the out-of-phase component (χ'') increases dramatically at all frequencies (Figure 3), with the magnitude of χ'' being frequency dependent. Due to the 2 K temperature limit of the instrument, a maximum in χ'' was not observed at frequencies as high as 1000 Hz. Nevertheless, these data support the assignment of **1** as a new member of the SMM family, expanding upon the recent report of the first f--d type SMM.[4] Unfortunately, as a result of the low blocking temperature ($T_B <$ 2 K) we did not observe hysteretic behavior in the magnetization of this sample. Additionally, two isostructural lanthanide analogues of this complex have been prepared and structurally characterized. Importantly, neither the Tb^{III} nor the Gd^{III} analogue exhibit an out-of-phase component in the ac experiment even though they retain high χT values at low temperatures (see Supporting Information). The lack of an out-of-phase ac magnetic susceptibility signal indicates that the SMM behavior is not solely a function of the manganese ions, nor can it be simply explained by invoking a magnetic phase transition or glassy magnetic behavior. Clearly, the molecular structure and the identity of the lanthanide ion are critical to the observed magnetic properties of these complexes.

In summary, we have synthesized a new lanthanide–transition-metal cluster complex with a high nuclearity of both types of metal ions, and initial magnetic measurements indicate that **1** is a member of the SMM family. Further studies at lower temperatures are required to understand more fully the interesting magnetic behavior of this complex. The results of these experiments and those of the various lanthanide analogues of **1** will be communicated in a future report.

Experimental Section

Complex **1** was prepared by the reaction of $Dy(NO_3)_3 \cdot 5H_2O$ (0.125 mmol), $Mn(O_2CCH_3)_2 \cdot 4H_2O$ (1 mmol), and salicylhydroxamic acid (1 mmol) in wet methanol (30 mL). The mixture was stirred overnight with a resulting brown solution and white precipitate. The precipitate was filtered, and the brown filtrate was allowed to slowly evaporate. Within three weeks, X-ray quality brown, needle crystals of **1** were obtained. We have repeated this synthesis with other lanthanide metal salts and obtained similar results.

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[1] a) D. Freedman, T. J. Emge, J. G. Brennan, *J. Am. Chem. Soc.* **1997**, *119*, 11112–11113; b) R. Wang, Z. Zheng, T. Jin, R. J. Staples, *Angew. Chem.* **1999**, *111*, 1929–1932; *Angew. Chem. Int. Ed.* **1999**, *38*, 1813–1815; c) M. R. Bürgstein, P. W. Roesky, *Angew. Chem.* **2000**, *112*, 559–562; *Angew. Chem. Int. Ed.* **2000**, *39*, 549–551; d) J. Xu, K. N. Raymond, *Angew. Chem.* **2000**, *112*, 2857–2859; *Angew. Chem. Int. Ed.* **2000**, *39*, 2745–2747; e) Y. Bretonnière, M. Mazzanti, J. Pécaut, M. M. Olmstead, *J. Am. Chem. Soc.* **2002**, *124*, 9012–9013; f) N. Fatin-Rouge, É. Tóth, D. Perret, R. H. Backer, A. Merbach, J.-C. G. Bünzli, *J. Am. Chem. Soc.* **2000**, *122*, 10810–10820; g) L. G. Westin, M. Kritikos, A. Caneschi, *Chem. Commun.* **2002**, 1012–1013.

[2] a) M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn, J. C. Trombe, *J. Am. Chem. Soc.* **1993**, *115*, 1822–1829; b) X.-M. Chen, S. M. J. Aubin, Y.-L. Wu, Y.-S. Yang, T. C. W. Mak, D. N. Hendrickson, *J. Am. Chem. Soc.* **1995**, *117*, 9600–9601; c) R. E. P. Winpenny, *Chem. Soc. Rev.* **1998**, *27*, 447–452; d) A. J. Stemmler, J. W. Kampf, M. L. Kirk, B. H. Atasi, V. L. Pecoraro, *Inorg. Chem.* **1999**, *38*, 2807–2817; e) C. Benelli, D. Gatteschi, *Chem. Rev.* **2002**, *102*, 2369–2387.

[3] a) R. A. Reyonlds III, D. Coucouvanis, *J. Am. Chem. Soc.* **1998**, *120*, 209–210; b) C. Benelli, M. Murrie, S. Parsons, R. E. P. Winpenny, *J. Chem. Soc. Dalton Trans.* **1999**, 4125–4126; c) B.-Q. Ma, S. Gao, O. Bai, H.-L. Sun, G.-X. Xu, *J. Chem. Soc. Dalton Trans.* **2000**, 1003–1004; d) B. Yan, Z. Chen, S. Wang, S. Gao, *Chem. Lett.* **2001**, 350–351; e) A. J. Tasiopoulos, T. A. O'Brien, K. A. Abboud, G. Christou, *Angew. Chem.* **2004**, *116*, 349–353; *Angew. Chem. Int. Ed.* **2004**, *43*, 345–349.

[4] S. Osa, T. Kido, N. Matsumoto, N. Re, A. Pochaba, J. Mrozinski, *J. Am. Chem. Soc.* **2004**, *126*, 420–421.

[5] M. S. Lah, V. L. Pecoraro, *J. Am. Chem. Soc.* **1989**, *111*, 7258–7259.

[6] C. Dendrinou-Samara, M. Alexiou, C. M. Zaleski, J. W. Kampf, M. L. Kirk, D. P. Kessissoglou, V. L. Pecoraro, *Angew. Chem.* **2003**, *115*, 3893–3896; *Angew. Chem. Int. Ed.* **2003**, *42*, 3763–3766.

[7] Crystals of **1** have been structurally characterized with the formula $[Dy_6Mn_6(H_2shi)_4(Hshi)_2(shi)_{10}(CH_3OH)_{10}(H_2O)_2](CH_3OH)_9(H_2O)_8$. Elemental Analysis calcd (%) for **1**: $C_{131}H_{170}N_{16}O_{77}Mn_6Dy_6$ (Fw = 4505.44) C 34.92; H 3.80; N 4.97; Found: C 34.82, H 3.69, N 4.92. Yield 15%. Crystal data for **1**: $M_r = 4505.44$, monoclinic, space group $C2/c$ (no. 15), $a = 34.292(5)$ Å, $b = 19.508(3)$ Å, $c = 27.666(4)$ Å, $\alpha = 90°$, $\beta = 102.475(5)°$, $\gamma = 90°$, $V = 18071(5)$ Å^{-3}, $Z = 4$; $\rho_{calc} = 1.655$ mg m^{-3}; $2.98° < \theta < 26.70°$; crystal dimensions (mm), $0.50 \times 0.18 \times 0.16$; $\mu = 2.943$ mm^{-1}; $T = 118(2)$ K; 18715 unique of 76992 reflections collected. 18715 reflections and 1083 parameters were used for the full matrix, least-squares refinement on F^2, $R1 = 0.0564$ $[I > 2\sigma(I)]$, $R1 = 0.0958$ (all data); $wR2 = 0.1576$ $[I > 2\sigma(I)]$, $wR2 = 0.1771$ (all data). Further details are given in the Supporting Information. CCDC-231260 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[8] 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) G. Christou, D. Gatteschi, D. N. Hendrickson, R. Sessoli, *MRS Bull.* **2000**, *25*, 66–71; c) D. Gatteschi, R. Sessoli, *Angew. Chem.* **2003**, *115*, 278–309; *Angew. Chem. Int. Ed.* **2003**, *42*, 268–297.

[9] N. Ishikawa, M. Sugita, T. Ishikawa, S.-Y. Koshihara, Y. Kaizu, *J. Am. Chem. Soc.* **2003**, *125*, 8694–8695.