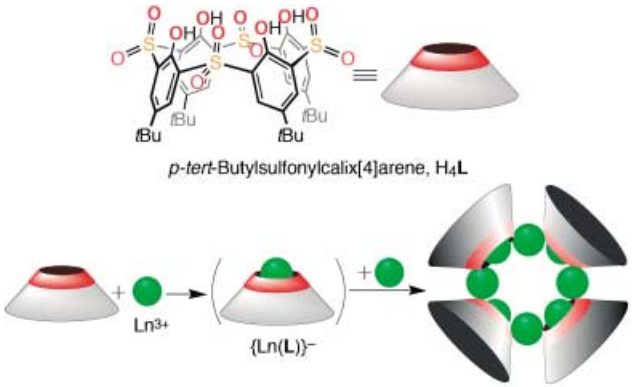
*Wheel Complexes*

# Octalanthanide Wheels Supported by *p-tert*-Butylsulfonylcalix[4]arene**

*Takashi Kajiwara,* Hashen Wu, Tasuku Ito,* Nobuhiko Iki,* and Sotaro Miyano*

Based on a bottom-up approach,[1] functionalized and structurally unique metal clusters with high nuclearity have been synthesized. Wheel-shaped clusters are one of the most highly symmetric architectures,[2] which often consist of first-row transition-metal ions.[2a–e] Lanthanide complexes have attracted considerable attention due to their practical properties.[3] However, multi-lanthanide complexes are rather rare.[2f,4] Thus our goal was to develop a new and rational synthetic method to realize lanthanide cluster complexes. As a cluster-forming ligand, we employed a sulfonylcalix[4]arene ($H_4$**L**) (Scheme 1). We have already shown that thiacalixarenes and their derivatives act as multinucleating[5a] or cluster-forming ligands.[6] Since lanthanides show strong affinity towards oxygen donors,[7] $H_4$**L** can act as a multidentate, multinucleating ligand via many oxygen sites.[5] Herein we report the syntheses, structures, and magnetic properties of lanthanide wheels, $[Ln_8(\mathbf{L})_4(AcO)_8(EtOH)_4(H_2O)_4]$ (Ln = Gd




***Scheme 1.*** Step-by-step formation of a lanthanide wheel via a mononuclear subunit $\{Ln(\mathbf{L})\}^-$.

[*] Dr. T. Kajiwara, Prof. H. Wu, Prof. T. Ito
Department of Chemistry, Graduate School of Science
Tohoku University, Aramaki Aoba-ku, Sendai 980-8578 (Japan)
Fax: (+81) 22-217-6548
E-mail: kajiwara@agnus.chem.tohoku.ac.jp
ito@agnus.chem.tohoku.ac.jp
Prof. N. Iki, Prof. S. Miyano
Department of Biomolecular Engineering, Graduate School of Engineering
Tohoku University, Aramaki Aoba-ku, Sendai 980-8579 (Japan)
Fax: (+81) 22-217-7293
E-mail: iki@orgsynth.che.tohoku.ac.jp

[**] This work was supported by a Grant-in-Aid for Scientific Research (Nos. 10149102 and 14342023) from the Ministry of Education, Culture, Science, Sports, and Technology, Japan, as well as by JSPS Research for the Future Program.

  DOI: 10.1002/ange.200353449 

(**1**), Sm (**1′**)) and $[Ln'_8(\mathbf{L})_4(AcO)_8(MeOH)_4(H_2O)_8]$ (Ln′ = Nd(**2**), Pr(**2′**)).

Reaction of $Gd(AcO)_3{\cdot}4H_2O$ and $H_4\mathbf{L}$ in a 2:1 ratio in EtOH/$CHCl_3$ gave crystals of **1** in good yield (87%). The complex (Figure 1) possesses a wheel-like core involving eight $Gd^{III}$ ions supported by four $\mathbf{L}^{4-}$ and eight $AcO^-$ groups. The diameter of the $Gd_8$ cluster core (Gd1···Gd1*) is ≈9.8 Å. The $\mathbf{L}^{4-}$ groups bridge three $Gd^{III}$ ions, thus acting as a tetradentate ligand for Gd1 and Gd3 via four $O_{phenoxo}$ atoms, and also acting as a bisbidentate chelating ligand for Gd2 and Gd4 via an $O_{phenoxo}$ and an $O_{sulfonyl}$ atom (Figure 2). The wheel involves

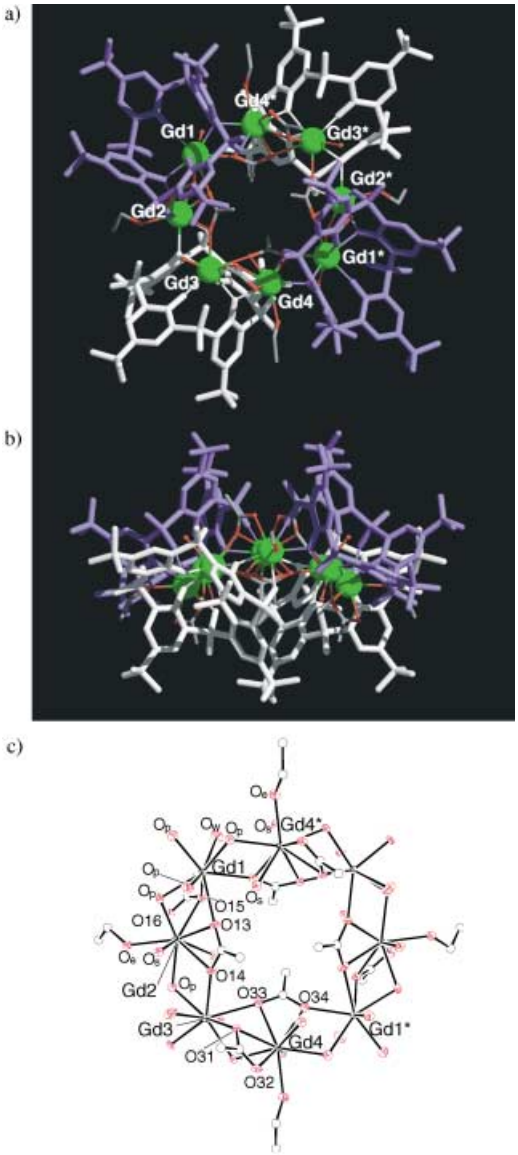



***Figure 1.*** Crystal structure of **1**. The molecule has a crystallographic twofold axis and half of the molecule is independent. a) Top view and b) side view of the molecule, where two crystallographically independent $\mathbf{L}^{4-}$ units are depicted in white and blue (Gd green, O red, C gray); c) ORTEP drawing of the $Gd_8$ core with thermal ellipsoids at 40% probability. Oxygen atoms from phenoxo and sulfonyl groups, ethanol, and water molecules are signified as $O_p$, $O_s$, $O_e$, and $O_w$, respectively. Selected atomic distances [Å]: Gd1-$O_p$ 2.230(3)–2.436(2), Gd1-O13 2.533(3), Gd1-O15 2.454(3), Gd1-O34* 2.384(3), Gd2-$O_p$ 2.354(2) and 2.377(3), Gd2-O13 2.483(3), Gd2-O14 2.454(2), Gd2-O15 2.434(3), Gd2-O16 2.384(3), Gd3-$O_p$ 2.227(2)–2.441(2), Gd3-O14 2.388(2), Gd3-O31 2.444(2), Gd3-O33 2.587(2), Gd4-$O_p$ 2.354(2) and 2.362(2), Gd4-O31 2.468(2), Gd4-O32 2.374(3), Gd4-O33 2.462(3), Gd4-O34 2.452(3), Gd1-Gd2 3.6826(5), Gd1-Gd4* 4.0120(5), Gd2-Gd3 3.9987(5), Gd3-Gd4 3.6960(5), Gd···Gd* 9.5006(12)–9.8539(9). Symmetry transformation (*): $-x+1, y, -z+1/2$.

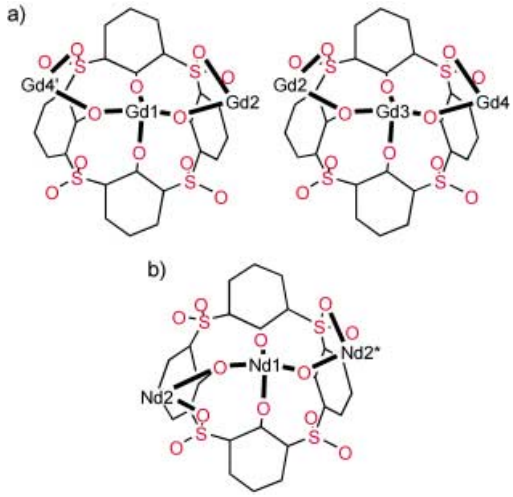



***Figure 2.*** Schematic diagrams of the bisbidentate/tetradentate chelation of $\mathbf{L}^{4-}$ in a) **1** and in b) **2**.

two kinds of $AcO^-$ ions, which both chelate to Gd2; one $AcO^-$ ion bridges Gd1/Gd2 via O15 in a $\mu_2$-$\kappa^1O$; $\kappa^2O,O'$ manner, and the other bridges Gd1/Gd2/Gd3 via O13 and O14 in a $\mu_3$-$\kappa^1O$; $\kappa^2O,O'$; $\kappa^1O'$ manner. The situation is similar at the Gd4 site. As a result, $Gd^{III}$ ions in sets of Gd1/Gd2 and Gd3/Gd4 are triply connected, whereas Gd2/Gd3 and Gd4/Gd1* are doubly connected. The $Gd^{III}$ octagon is slightly bent (Figure 1b) giving deviations from the ideal plane of −0.97 Å for Gd2 and 0.98 Å for Gd4. Gd1 and Gd3 are octacoordinated and Gd2 and Gd4 are nonacoordinated, with each coordination sphere completed by terminal ligands such as EtOH and $H_2O$. Using $Sm(AcO)_3{\cdot}4H_2O$ instead of $Gd(AcO)_3{\cdot}4H_2O$, a $Sm_8$ wheel **1′** was also obtained (95% yield) which is isostructural to **1** ($Sm{-}O_{phenoxo}$ = 2.255(3)–2.509(3) Å).[8]

A similar reaction of $Nd(AcO)_3{\cdot}4H_2O$ and $H_4\mathbf{L}$ in 2:1 ratio in EtOH/$CHCl_3$ followed by recrystallization from MeOH/$CHCl_3$ gave crystals of $[Nd_8(\mathbf{L})_4(AcO)_8(MeOH)_4(H_2O)_8]$ (**2**). The structure of **2** is similar to **1** (Figure 3) except that **2** crystallized in a tetragonal crystal system and only 1/8 of the molecule is crystallographically independent. The $\mathbf{L}^{4-}$ ion acts as a tetradentate ligand for Nd1 via four $O_{phenoxo}$ linkages, and also acts as a bisbidentate ligand for Nd2 and Nd2* via an $O_{phenoxo}$ atom and an $O_{sulfonyl}$ atom (Figure 2). The $Nd_8$ cluster core is completed by eight acetate groups in either a $\mu_2$-$\kappa^1O$; $\kappa^1O'$ or a $\mu_3$-$\kappa^1O$; $\kappa^2O,O'$; $\kappa^1O'$ manner. The diameter of the $Nd_8$ core is ≈10.5 Å. In **2**, the $Nd_8$ core is flatter than the $Gd_8$ core in **1** (Figure 3), with a deviation from the ideal plane of 0.2296(2) Å for Nd1. A $Pr_8$ wheel **2′** was also obtained by the use of $Pr(AcO)_3{\cdot}4_2O$ (32%

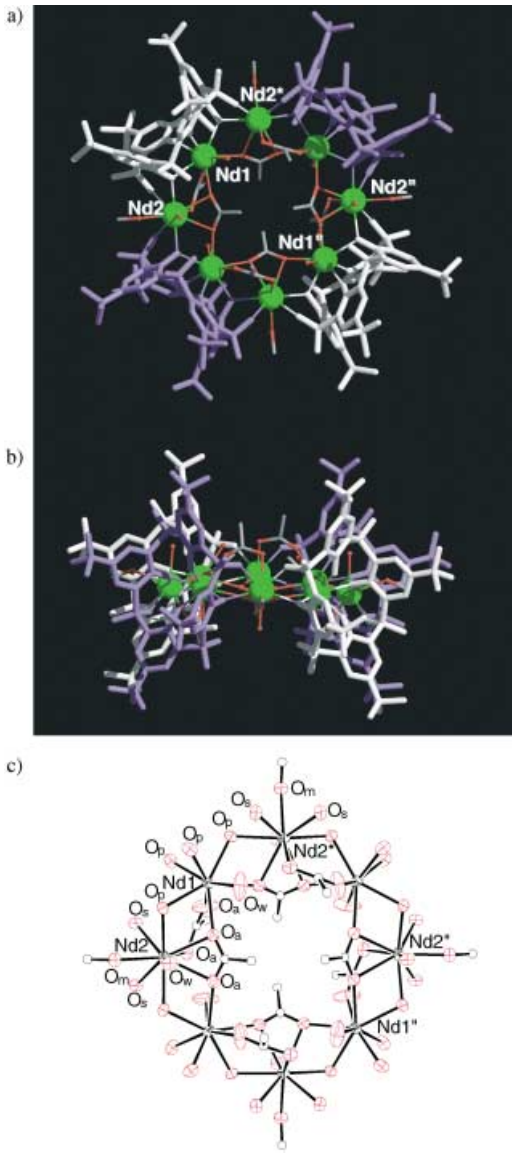



***Figure 3.*** Crystal structure of **2**. a) Top view and b) side view of the molecule where adjoining $L^{4-}$ ligands are discriminated in white and blue; c) ORTEP drawing of the $Nd_8$ core with thermal ellipsoids at 40% probability. Oxygen atoms from acetate, phenoxo, and sulfonyl groups, methanol, and water molecules are signified as $O_a$, $O_p$, $O_s$, $O_m$, and $O_w$, respectively. Selected atomic distances [Å]: Nd1-$O_p$ 2.3274(16) and 2.4699(14), Nd1-$O_a$ 2.460(2) and 2.4860(17), Nd2-$O_p$ 2.4824(15), Nd2-$O_a$ 2.464(2) and 2.5879(17), Nd1-Nd2 4.0713(3), Nd1···Nd1″ 9.9269(8), Nd2···Nd2″ 11.1205(9). Symmetry transformations: * $y+1/2, -x, -z+1/2$, ″ $x+1/2, -y-1/2, z$.

yield), which is isostructural to **2** ($Pr-O_{phenoxo} = 2.334(2)$ and 2.4835(18) Å).[8]

Complexes **1** and **2** showed slight differences in their core structures mainly because of the coordination distances between the phenoxo oxygen atoms and a lanthanide ion (Gd2, Gd4, or Nd2). Since the heavier $Gd^{III}$ is slightly smaller than $Nd^{III}$ in terms of atomic radius, shorter $Gd-O_{phenoxo}$ bonds (2.354(2)–2.377(3) Å) make the cluster core crowded, and thus the core is bent to avoid close contact of methyl groups and $\mu_3$-bonded acetate groups. On the other hand, longer $Nd-O_{phenoxo}$ bonds (2.4824(15) Å) permit the flatter wheel core found in **2**.

Scheme 1 shows a proposed mechanism for the formation of the lanthanide wheels. The wheels appear to form by a "step-by-step" complexation process. Since a calix[4]arene acts as a tetradentate ligand toward the large metal ions via four phenoxo oxygen atoms,[9] the reaction of a lanthanide with $H_4$**L** will give first a cone-shaped mononuclear subunit, $\{Ln(\mathbf{L})\}^-$, which can act as a "metal-involving ligand" via phenoxo and sulfonyl oxygen atoms, which are directed outwards from the cone. Reaction with another equivalent of a metal ion results in the formation of the cyclic tetramer $\mathbf{L}^{4-}$. In this cyclization process, sulfonyl oxygen atoms bond to a second Ln ion in a $\{Ln(\mathbf{L})\}^-$ subunit. The presence of a $Gd^{III}$ subunit in the reaction solution was confirmed by the ESI mass spectrometry, which showed a parent peak centered around $m/z$ 1001.6, which corresponds to $\{Gd(\mathbf{L})\}^-$. Moreover, the subunit was isolated as a less-soluble dimer, $(Bu_4N)_2[\{Gd(\mathbf{L})(H_2O)_2\}_2]$ (**3**, Figure 4).[8] In **3**, $\mathbf{L}^{4-}$ is tetradentate, and two $O_{phenoxo}$ atoms bridge adjoining $Gd^{III}$ ions to form a dimer. The subunits act as a "metal-involving ligand" via an $O_{phenoxo}$ atom and an $O_{sulfonyl}$ atom.

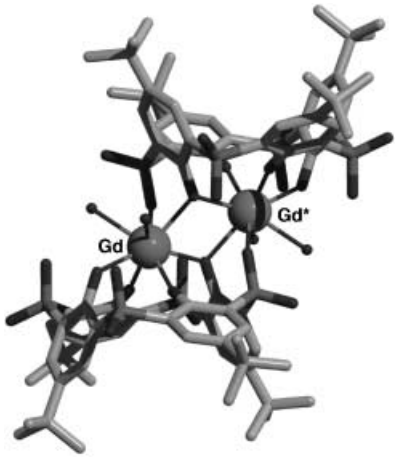



***Figure 4.*** Crystal structure of $[\{Gd(\mathbf{L})(H_2O)_2\}_2]^{2-}$. Symmetry transformation: * $-x+2, -y, -z$.

The magnetic properties of the wheel clusters were briefly examined (Figure 5). The $\chi_m T$ value of **2** shows a continuous decrease when the temperature is lowered, which is mainly due to spin–orbit interactions[10] and are difficult to analyze. On the other hand, **1** shows a simple temperature dependence indicating weak antiferromagnetic interactions among $Gd^{III}$ ions. The system is too large to handle with the Heisenberg model, hence the magnitude of the interaction was estimated based on the Curie–Weiss model, and was found to be −2.1(1) K.[11] Each of the adjoining $Gd^{III}$ ions are doubly or triply connected by oxygen atoms, and the slight overlap of magnetic orbitals causes the weak antiferromagnetic interaction.

We have presented a novel and rational synthetic method for the synthesis of lanthanide wheels using sulfonylcalix[4]-arene as a cluster-forming ligand. The introduction of sulfonyl

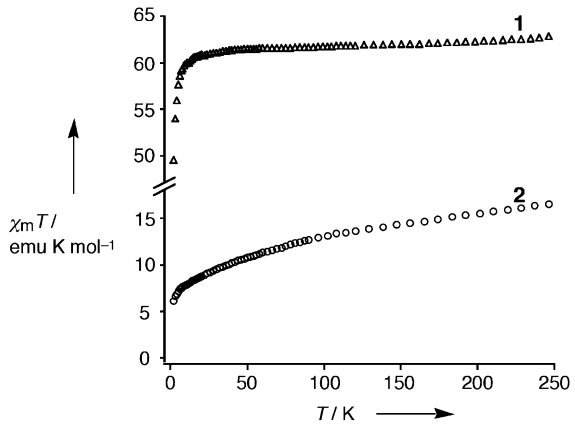



***Figure 5.*** Plots of $\chi_m T$ versus $T$ for **1** (△) and **2** (○).

groups on the calix[4]arene rim makes it possible to form the lanthanide wheels. The structures of the four wheels are similar, and other lanthanide ions can be expected to form similar wheel structures. Reactions with other lanthanide ions are currently being explored as well as the synthesis of mixed-metal clusters.

## *Experimental Section*

**1**: $H_4$**L** (42.5 mg, 0.05 mmol) and $Gd(AcO)_3{\cdot}3H_2O$ (40.0 mg, 0.1 mmol) in EtOH/$CHCl_3$ (1:1 (v/v), 20 mL) were refluxed for 15 min and then the solution was evaporated to dryness. The resulting white residue was then recrystallized from the same solvent, and colorless blocks of **1**·8 EtOH·4 $H_2O$ were obtained over several days (87%).

**2**: $H_4$**L** (42.5 mg, 0.05 mmol) and $Nd(AcO)_3{\cdot}3H_2O$ (40.0 mg, 0.1 mmol) in EtOH/$CHCl_3$ (1:1 (v/v), 20 mL) were refluxed for 15 min and then the solution was evaporated to dryness. The resulting white residue was recrystallized from MeOH/$CHCl_3$ (1:1 v/v), and colorless blocks of **2**·4 MeOH·24 $H_2O$ were obtained (40%).

Crystal data for **1** ($C_{200}H_{288}Gd_8O_{84}S_{16}$; $M_r = 5807.26$): colorless prism, orthorhombic, space group *Pbcn*, $a = 38.918(5)$, $b = 16.013(2)$, $c = 43.692(6)$ Å, $V = 27228(6)$ Å$^3$, $Z = 4$, $T = 200$ K, $\rho_{calcd} = 1.417$ g cm$^{-3}$, $F(000) = 11712$, $\mu(Mo_{K\alpha}) = 2.117$ mm$^{-1}$. Crystal data for **2** ($C_{184}H_{296}Nd_8O_{104}S_{16}$; $M_r = 5839.09$): colorless prism, tetragonal, space group $P4_2/nnm$, $a = 29.043(2)$, $c = 19.589(2)$ Å, $V = 16523(3)$ Å$^3$, $Z = 2$, $T = 240$ K, $\rho_{calcd} = 1.174$ g cm$^{-3}$, $F(000) = 5936$, $\mu(Mo_{K\alpha}) = 1.402$ mm$^{-1}$. Data were collected on a Bruker SMART CCD diffractometer ($Mo_{K\alpha}$, $\lambda = 0.71073$ Å). Complete hemispheres of data were collected using $\omega$-scans. Integrated intensities were obtained with SAINT+[12] and SADABS[12] was used for absorption correction. The structures were solved by direct methods using SHELXS-97[12] and refined by least-squares on $F^2$, SHELXL-97,[12] to give for **1**: using 1364 parameters, $wR_2 = 0.2070$ (23414 unique reflections), $R_1 = 0.0781$ (15153 reflections with $I > 2\sigma(I)$); for **2**: using 368 parameters, $wR_2 = 0.1945$ (9791 unique reflections), $R_1 = 0.0544$ (6400 reflections with $I > 2\sigma(I)$). CCDC-225414 and -225415 contain 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).

Received: December 3, 2003 [Z53449]

**Keywords:** calixarenes · cluster compounds · lanthanides · macrocycles · magnetic properties


[1] V. Balzani, A. Credi, M. Venturi, *Chem. Eur. J.* **2002**, *8*, 5525.

[2] See for example: a) A. Caneschi, A. Cornia, S. J. Lippard, *Angew. Chem.* **1995**, *107*, 511; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 467; b) C. Cadiou, M. Murrie, C. Paulsen, V. Villar, W. Wernsdorfer, R. E. P. Winpenny, *Chem. Commun.* **2001**, 2666; c) A. Caneschi, A. Cornia, A. C. Fabretti, D. Gatteschi, *Angew. Chem.* **1999**, *111*, 1372; *Angew. Chem. Int. Ed.* **1999**, *38*, 1295; d) H. Oshio, N. Hoshino, T. Ito, M. Nakano, F. Renz, P. Gütlich, *Angew. Chem.* **2003**, *115*, 233; *Angew. Chem. Int. Ed.* **2003**, *42*, 223; e) F. K. Larsen, E. J. L. McInnes, H. E. Mkani, J. Overgaard, S. Piligkos, G. Rajaraman, E. Rentschler, A. A. Smith, G. M. Smith, V. Boote, M. Jennings, G. A. Timco, R. E. P. Winpenny, *Angew. Chem.* **2003**, *115*, 105; *Angew. Chem. Int. Ed.* **2003**, *42*, 101; f) J. Xu, K. N. Raymond, *Angew. Chem.* **2000**, *112*, 2857; *Angew. Chem. Int. Ed.* **2000**, *39*, 2745; g) A. Müller, E. Krickemeyer, J. Meyer, H. Bögge, F. Peters, W. Plass, E. Diemann, S. Dillinger, F. Nonnenbruch, M. Randerath, C. Menke, *Angew. Chem.* **1995**, *107*, 2293; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2122.

[3] a) D. Parker, J. A. G. Williams, *J. Chem. Soc. Dalton Trans.* **1996**, 3613; b) P. Caravan, J. J. Ellison, T. J. McMurry, R. B. Lauffer, *Chem. Rev.* **1999**, *99*, 2293; c) S. T. Hatscher, W. Urland, *Angew. Chem.* **2003**, *115*, 2969; *Angew. Chem. Int. Ed.* **2003**, *42*, 2862.

[4] a) G. Xu, Z.-M. Wang, Z. He, Z. Lu, C.-S. Liao, C.-H. Yan, *Inorg. Chem.* **2002**, *41*, 6802; b) R. Wang, Z. Zheng, T. Jin, R. J. Staples, *Angew. Chem.* **1999**, *111*, 1929; *Angew. Chem. Int. Ed.* **1999**, *38*, 1813.

[5] a) T. Kajiwara, S. Yokozawa, T. Ito, N. Iki, N. Morohashi, S. Miyano, *Chem. Lett.* **2001**, 6; b) T. Kajiwara, S. Yokozawa, T. Ito, N. Iki, N. Morohashi, S. Miyano, *Angew. Chem.* **2002**, *114*, 2180; *Angew. Chem. Int. Ed.* **2002**, *41*, 2076.

[6] a) T. Kajiwara, N. Kon, S. Yokozawa, T. Ito, N. Iki, S. Miyano, *J. Am. Chem. Soc.* **2002**, *124*, 11274; b) T. Kajiwara, R. Shinagawa, T. Ito, N. Iki, S. Miyano, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2267.

[7] F. A. Hart in *Comprehensive Coordination Chemistry*, *Vol. 3* (Ed.: G. Wilkinson), Pergamon, Oxford, **1987**, pp. 1073–1081.

[8] Crystal data for **1′**: colorless prism, orthorhombic, space group *Pbcn*, $a = 39.070(5)$, $b = 15.972(2)$, $c = 43.998(7)$ Å, $V = 27456(7)$ Å$^3$, $Z = 4$, $R_1 = 0.0914$. Crystal data for **2′**: colorless prism, tetragonal, space group $P4_2/nnm$, $a = 29.118(4)$, $c = 19.550(4)$ Å, $V = 16576(4)$ Å$^3$, $Z = 2$, $R_1 = 0.0650$. Crystal data for **3**: colorless prism, monoclinic, space group $P2_1/n$, $a = 17.2391(18)$, $b = 14.6013(15)$, $c = 26.650(3)$ Å, $\beta = 95.779(3)°$, $V = 6674.1(12)$ Å$^3$, $Z = 2$, $R_1 = 0.0463$. CCDC-230568 to -230570 contain the supplementary crystallographic data for these complexes. For more details, also see Supporting Information.

[9] a) J. Attner, U. Radius, *Chem. Eur. J.* **2001**, *7*, 783; b) Z. Asfari, A. Bilyk, J. W. C. Dunlop, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, B. W. Skelton, A. H. White, *Angew. Chem.* **2001**, *113*, 744; *Angew. Chem. Int. Ed.* **2001**, *40*, 721.

[10] M. L. Kahn, C. Mathonière, O. Kahn, *Inorg. Chem.* **1999**, *38*, 3692.

[11] O. Kahn, *Molecular Magnetism*, VCH, New York, **1993**.

[12] SHELXTL-PC Package. Bruker, AXS Inc., Madison, Wisconsin, USA, **1998**.