Two $Mn^{II}_2Ln^{III}_4$ (Ln = Gd, Eu) hexanuclear compounds of *p-tert*-butylsulfinylcalix[4]arene†

Yanfeng Bi,[a,c] Xiu-Teng Wang,[b] Bing-Wu Wang,[b] Wuping Liao,*[a] Xiaofei Wang,[a,c] Hongjie Zhang,[a] Song Gao*[b] and Deqian Li[a]

Two 3d-4f heterometallic compounds of *p-tert*-butylsulfinylcalix[4]arene were synthesized by the solvothermal method and characterized by some hinged double-dumbbell-like subunits in which two perpendicular dumbbell entities were constructed by an in-between isosceles triangle $Mn^{II}Ln^{III}_2$, and two tail-to-tail calixarene molecules, and hinged by the lanthanide–sulfinyl group bonding. The magnetic properties of the title compounds were examined.

Introduction

3d-4f Heterometallic complexes have attracted considerable attention[1,2] because of their magnetic properties since Gatteschi *et al.* reported ferromagnetic coupling between Gd[III] and Cu[II] in two Cu₂Gd trinuclear compounds.[3,4] Although a series of copper–lanthanide compounds[5] have been synthesized successfully and characterized, there are few reports on Mn–Ln complexes.[6,7] Most recently, our group reported a 3d-4f $Mn^{II}_2Gd^{III}_2$ tetranuclear cluster of *p-tert*-butyltetrathiacalix-[4]arene (TC4A).[8] On the other hand, *p-tert*-butylsulfinylcalix[4]arene (H₄**L**, Scheme 1) bearing

eight adjacent oxygen atoms at the lower rim and the bridgings, has proved to be a potential candidate to give polynuclear complexes with limited transition metal ions. For instance, Luneau and co-worker reported a Mn^{II}_4 core which can be regarded as a manganese square sandwiched between two **L** ligands,[9] and Iki *et al.* obtained a Pd[II]₂ compound involving 1,2- and 1,3-alternate **L**, and a Cu[II]₄ core with all stereoisomers of **L**.[10,11] However, to our best knowledge, there are no reports on lanthanide complexes or 3d-4f heterometallic compounds incorporating *p-tert*-butylsulfinylcalix[4]arene.[12] Our interest was focused on preparing new 3d-4f heterometallic complexes using this ligand for magnetic studies. Herein we report the syntheses, structures, and magnetic properties of two unprecedented $Mn^{II}_2Ln^{III}_4$ compounds, namely, [Mn₂Ln₄(**L**)₄(H₂O)₂]·(H₂O)$_m$ (CHCl₃)$_n$ (Ln = Gd, m = 6.3, n = 7.7 for **1**, and Ln = Eu, m = 5.3, n = 7.6 for **2**).

Compounds **1** and **2** were synthesized by the solvothermal method as we described previously.[8] The reaction of the multidentate ligand H₄**L** with two equivalents of Mn(Ac)₂·4H₂O and one equivalent of Ln(Ac)₃·4H₂O (Ln = Gd for **1**, and Eu for **2**) in a 1 : 1 chloroform–methanol mixed solvent with several drops of water afforded the title compounds in good yields. Single-crystal X-ray diffraction determination reveals that isostructural compounds **1** and **2** are constructed by supramolecular stacking of some isolated hinged double-dumbbell-like subunits in which the dumbbells contain two tail-to-tail calixarenes and an in-between triangular $Mn^{II}Ln^{III}_2$ cluster, and are hinged by the bonding between the lanthanide and the bridging sulfinyl groups.

Scheme 1 *p-tert*-Butylsulfinylcalix[4]arene (H₄**L**).

[a]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China. E-mail: wpliao@ciac.jl.cn; Fax: +86-431-8569-8041; Tel: +86-431-8526-2036
[b]Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China. E-mail: gaosong@pku.edu.cn; Fax: +86-10-6275-1708; Tel: +86-10-6275-1708
[c]Graduate University of the Chinese Academy of Sciences, Beijing, 100049, China

Experimental

Materials and instrumentation

p-tert-Butylsulfinylcalix[4]arene (H₄**L**) was synthesized as reported in the literature,[13] and the other reagents were purchased from commercial sources and used as received. Mn and Gd analyses were determined by a HITACHI S-4800 scanning electron microscope. Magnetic susceptibility measurements for **1** and **2** were performed on a Quantum Design MPMS XL-5 SQUID system in the range of 2–300 K. Diamagnetic corrections for the sample and sample holder were applied to the data.

Synthesis

1 and **2**: Colorless block-shaped crystals of compound **1** and yellow crystals of **2** were obtained from the mixture of *p-tert*-butylsulfinylcalix[4]arene (0.081 g, 0.1 mmol), $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.049 g, 0.2 mmol), $Ln(CH_3COO)_3 \cdot 4H_2O$ (Ln = Gd for **1** and Eu for **2**, 0.06 g, *ca.* 0.15 mmol), $CHCl_3$ (5 ml), CH_3OH (5 ml) and several drops of water in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to 20 °C at about 4 °C h^{-1}. The crystals were isolated by filtration and then washed with methanol and chloroform. Yield: *ca.* 65% for both compounds with respect to calixarene. The EDS analysis of **1** reveals that the molar ratio of Mn to Gd molar is 1 : 2.01, comparable with the expected 1 : 2.

X-Ray crystallography

The X-ray intensity data for compounds **1** and **2** were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) operated at 2.0 kW (50 kV, 40 mA). The crystal structure was solved by means of Direct Methods and refined employing full-matrix least squares on F^2 (SHELXTL-97).[14] All the non-hydrogen atoms were refined anisotropically except some isolated molecular atoms. The sulfinyl oxygen atom (O5) was refined with two disordered sites (O5 and O5′) both with the occupation factor being of 0.5. Unfortunately, it was not possible to locate all hydrogen atoms on water molecular (O9, O10, O11) from the Fourier difference map for this to be clarified. In addition, the high R_1 and wR_2 factor of compounds **1** and **2** are due to the weak crystal diffraction quality and the disorder of the solvent molecules. Therefore the crystal structures treated by the "SQUEEZE" method as implemented in PLATON[15] are presented here and those unsqueezed are available in the ESI (see Table 1 and ESI for details).†

Table 1 Crystallographic data obtained by the refinement using the "SQUEEZE" command in PLATON for compounds **1–2**

	1-Squeezed	**2**-Squeezed
Formula	$C_{160}H_{176}Gd_4Mn_2O_{34}S_{16}$	$C_{160}H_{176}Eu_4Mn_2O_{34}S_{16}$
Formula wt.	3894.85	3873.69
Crystal system	Tetragonal	Tetragonal
Space group	$I4_1/a$	$I4_1/a$
a/Å	19.7575(6)	19.6997(8)
b/Å	19.7575(6)	19.6997(8)
c/Å	65.511(3)	65.255(4)
V/Å^3	25572.8(16)	25324(2)
Z	4	4
D_c/g cm^{-3}	1.012	1.016
μ/mm^{-1}	1.295	1.251
$F(000)$	7880	7864
Tot. data	124362	256781
Uniq. data	14640	15242
R_{int}	0.030	0.055
GOF	1.075	1.028
$R_1{}^a[I > 2\sigma(I)]$	0.0413	0.0430
w$R_2{}^b$(all data)	0.1195	0.1204

^{a} $R_1 = \sum \|F_0| - |F_c\|/\sum |F_0|$. ^{b} w$R_2 = \sum[w(F_0{}^2 - F_c{}^2)^2]/\sum[w(F_0{}^2)^2]^{1/2}$.

Description of structure

In the structures, there are two different crystallographic positions found for the metal atoms, Mn1 and Ln1 (Fig. 1). Mn1 is coordinated by four phenoxyl oxygen atoms (O1, O1A, O4, and O4A), two halves of sulfinyl oxygen atoms (O5 and O5A), and a μ$_3$-OH$_2$ (O9) with Mn–O distances being of 2.096(5)–2.234(3) Å. The bond lengths and angles (Table S1†) are similar to those reported in the monometallic Mn^{II}–**L** complex.[9] The lanthanide cation is surrounded by eight oxygen atoms from four phenoxyl groups, three sulfinyl groups from three different **L** ligands, and a μ$_3$-OH$_2$, and all the bond lengths and angles are located in the normal range.[16] Mn1, Ln1 and Ln1A generated by a reflection operation on Ln1 form an isosceles triangle trinuclear core (shown in Fig. 2) with the Mn–Ln/Ln–Ln distances being of 3.31/4.73 Å for **1**, and 3.31/4.75 Å for **2**, and the Mn–Ln–Ln/Ln–Mn–Ln angles being of 44.39/91.22° for **1**, and 44.19/91.61° for **2**, respectively. Furthermore, the trinuclear core is bonded by two tail-to-tail **L** ligands to form a dumbbell-like entity. The dihedral angle between two planes formed by the bridging sulfur atoms of the upper and bottom calixarenes is *ca.* 7° which is smaller than that in the Mn$^{II}_2$Gd$^{III}_2$-(TC4A)$_2$ sandwich (*ca.* 14°).[8] The smaller dihedral angle may be reasoned to the fact that the metals are bonded to the oxygen atoms of the bridging sulfinyl groups but not to S atoms as in the Mn$^{II}_2$Gd$^{III}_2$-(TC4A)$_2$ sandwich,[8] which suggests that the coordination of metals to sulfinyl S or O atoms is not governed by the metal-donor affinity but by stereochemistry.[11] By another
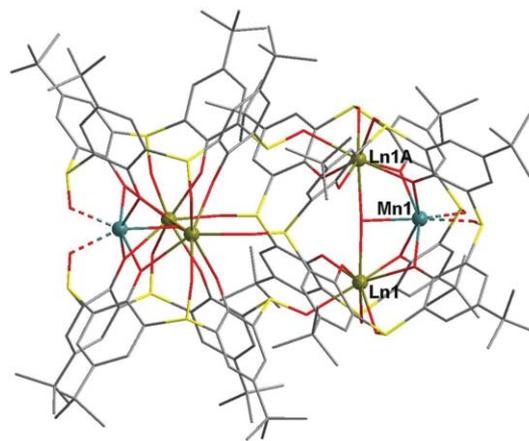

Fig. 1 Molecular structures of isostructural compounds **1** and **2**. The hydrogen atoms and solvent molecules are omitted for clarity.
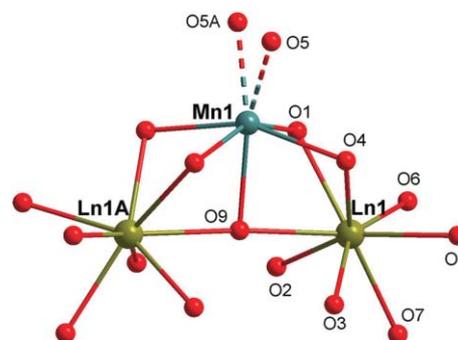

Fig. 2 Ball-and-stick representation of an isosceles triangle Mn^{II}Ln$^{III}_2$ core.

4-fold rotoinversion operation along the axis perpendicular to the dumbbell, another dumbbell-like entity has been generated and then these two dumbbells are hinged by the bonding between lanthanides and sulfinyl groups to form a Mn_2Ln_4–L_4 hexanuclear subunit. Within these hexanuclear subunits, the shortest M–M distance between two trinuclear entities reaches *ca.* 7.63 Å, that is, these two trinuclear entities are well separated by a void of *ca.* 5.78 Å in diameter based on the nearest opposite sulfur atoms.

In the extended structures, the hinged double-dumbbell subunits are well separated from each other by the solvent water and chloroform molecules. They are stacked together by van der Waals forces. In addition, according to the definition of four possible stereoisomer configurations (*rccc*, *rcct*, *rctt*, and *rtct*, where *r* = reference S=O group, *c* = *cis*, and *t* = *trans*) of sulfinylcalix[4]arene suggested by Iki *et al.*,[11,17] one can find that a part of the **L** ligands should adopt *rcct* configuration while the others adopt *rtct* configuration due to the disordered O5 site.

Magnetic susceptibility measurements

Magnetic susceptibility measurements for **1** and **2** have been performed in the range of 2–300 K. The temperature dependencies of $\chi_M T$ and χ_M^{-1} of **1** are presented in Fig. 3. For **1**, the experimental $\chi_M T$ at 300 K are 39.62 cm³ K mol⁻¹ which is in agreement with the presence of two Mn^{II} ions (4.375 cm³ K mol⁻¹ expected for $g = 2$) and four Gd^{III} ions (7.875 cm³ K mol⁻¹ with $g = 2$).[1,6] Upon cooling, the $\chi_M T$ value decreases slightly to 38.91 cm³ K mol⁻¹ at 100 K, and then decreases dramatically to 21.92 cm³ K mol⁻¹ at 2 K, suggesting that the compound has a large ground-state spin value. The susceptibility data of **1** above 20 K obeys the Curie–Weiss law with the Curie constant $C = +40.1$ cm³ K mol⁻¹ and the Weiss constant $\theta = -3.92$ K, which indicates dominant antiferromagnetic interactions between the metals. Because of the long distance between the two trinuclear entities in an isolated hexanuclear double-dumbbell, the hexamer of compound **1** can be viewed as two $MnGd_2$ trimers and the overall antiferromagnetic interactions exist in the trinuclear entity. Considering the topology and connectivity, there are two different magnetic interactions within the $MnGd_2$ trimer, namely, J_1 and J_2, representing the couplings between Mn and Gd, Gd and Gd,
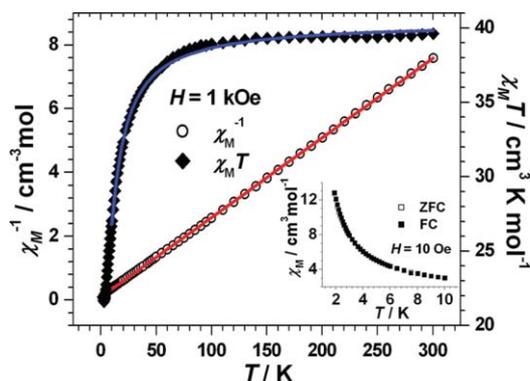
respectively. The Heisenberg spin Hamiltonian was used for an isotropic exchange coupling approximately with $S_{Mn} = 5/2$ and $S_{Gd} = 7/2$.

$$H = -2J_1(S_{Mn1}S_{Gd1} + S_{Mn1}S_{Gd1A}) - 2J_2 S_{Gd1} S_{Gd1A}$$

The magnetic data are simulated by a least-squares fitting MAGPACK program[18] with a full-matrix diagonalization of exchange coupling. The best parameters in the range of 10 to 300 K are obtained: $J_1 = -0.263$ cm⁻¹, $J_2 = -0.091$ cm⁻¹, $g = 2.005$ with $R = 2.5 \times 10^{-5}$ $[R = [\sum(\chi_{obs} - \chi_{calc})^2/\sum(\chi_{obs})^2]$. Similar intramolecular antiferromagnetic interaction was also observed in other Mn–Gd compounds.[6,7] The blue solid line in Fig. 3 represents the simulation. The signs of the exchange couplings and the estimated values indicate AF couplings through the two phenoxyl oxygen bridges and the μ_3-OH_2 connections. Thus spin frustration plays an important role in the $MnGd_2$ trimer unit since the triangular arrangement of coupled metal ions is the textbook topology for this competing effect. At the lowest temperature the $\chi_M T$ value is fairly large, not close to zero, suggesting that the compound has a large ground-state spin value. The ground state of **1** may be a mixture of a series of spin states due to a high density of spin states and/or the presence of spin frustration effects.[19]

The temperature dependencies of the zero-field cooled and the field-cooled magnetization were measured at a low field of 10 Oe (Fig. 3, inset). No divergence of the ZFC and FC plots was observed. Moreover, in non frequency-dependent ac susceptibility data no peaks were observed (Fig. S2†). All these results revealed neither long-range ordering nor single molecule magnet behavior above 1.9 K.

We investigated the variation of the magnetization M with the applied magnetic field H for **1** in the range 0–50 kOe at 1.9 K (Fig. 4). The initial increase of magnetization is relatively rapid with field up to 10 kOe, and then becomes almost linear with a smaller slope up to 26.9 Nβ per Mn_2Gd_4 unit at 50 kOe, far from the saturation sum value of two Mn^{II} and four Gd^{III} ions, suggesting the AF coupling between metal ions. No hysteresis loop is observed, in agreement with the ZFC-FC measurement.
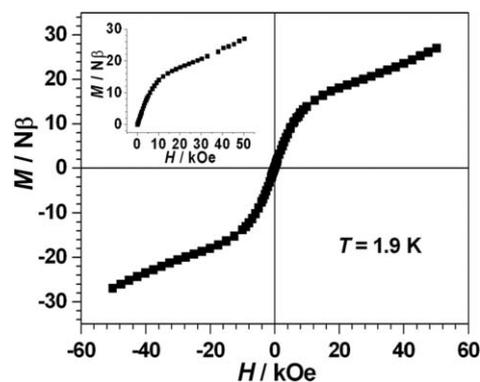

Fig. 4 The field-dependencies of magnetization of **1** at 1.9 K. Inset: the *M*–*H* plot at 1.9 K.

Fig. 3 Plots of $\chi_M T$ *vs.* *T* and $1/\chi_M$ *vs.* *T* for **1**. The red solid line represents the Curie–Weiss fitting and the blue one is the best fitting of magnetic susceptibilities calculated by MAGPACK. Inset: the ZFC-FC plot of **1** at 10 Oe.

For **2**, the observed $\chi_M T$ value at room temperature is 14.80 cm³ K mol⁻¹, which is consistent with the calculated value 14.7 cm³ K mol⁻¹ of two Mn^{II} ions and four Eu^{III} ions (1.50 cm³ K mol⁻¹ calculated by the Van Vleck equation allowing for population of the excited state[20]) (Fig. 5). The ^7F ground term of Eu^{III} is split
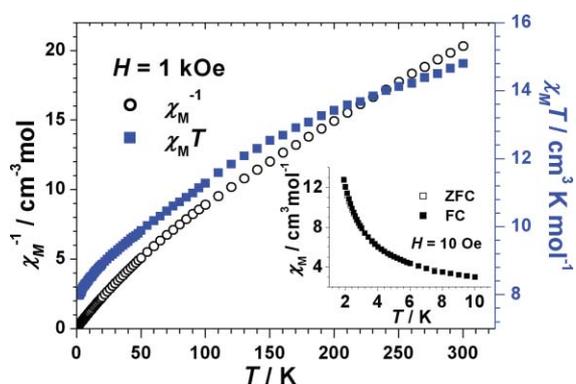
Fig. 5 Plots of $\chi_M T$ vs. T and $1/\chi_M$ vs. T for **2**. Inset: the ZFC-FC plot of **2** at 10 Oe.

into seven states due to the spin–orbit coupling, and the energy gap of these states are small enough that the excited states may be thermally populated at room temperature and above. As a result of the progressive depopulation of the Stark levels for the Eu^{III} ions, lowering the temperature induces a continuous decrease of the $\chi_M T$ value. The susceptibility data above 200 K obeys the Curie–Weiss law because of the presence of thermally populated excited states of Eu^{III} ions and the magnetic behavior of the two isolated Mn^{II} ions. At the lowest temperature, $\chi_M T$ is 8.0 cm³ K mol⁻¹, slightly lower than the expected value of two independent Mn^{II} ions owing to the magnetic saturation effect, indicating a $J = 0$ ground state of the Eu^{III} ion ($^7F_0$). In compound **2**, Eu^{III} ions have no unpaired electrons and have no spin–spin couplings with the Mn^{II} ions. Therefore the theoretical calculation to evaluate the magnetic interactions for this compound was avoided.

ZFC-FC measurements at low field displayed no irreversibility above 1.9 K (Fig. 5 inset). Moreover, in non-frequency-dependent ac susceptibility data no peaks were observed (Fig. S3†). All these results revealed neither long-range ordering nor single-molecule magnet (SMM) behavior above 1.9 K.

The magnetization M with the applied magnetic field H for **2** in the range 0–50 kOe at 1.9 K is shown in Fig. 6. The M–H plot shows a gradual increase with H and the magnetization is 9.6 Nβ at 50 kOe, slightly lower than the saturation value of two Mn^{II} ions, indicating the zero ground state of Eu^{III}. No hysteresis loop is observed.
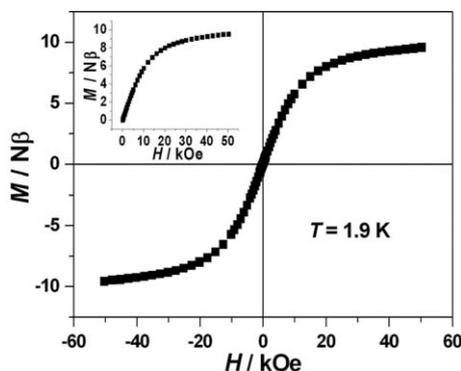

Fig. 6 The field-dependencies of magnetization of **2** at 1.9 K. Inset: the M–H plot at 1.9 K.

In summary, two isostructural heterometallic compounds **1** and **2** have been successfully synthesized and structurally characterized, representing the first examples of 3d-4f heterometallic compounds constructed from *p-tert*-butylsulfinylcalix[4]arene. The structures are featured by some isolated hinged double-dumbbell-like hexanuclear subunits which contain two hinged perpendicular dumbbell entities and two bridged in-between triangle Mn^{II}Ln^{III}_2 clusters. This work provides another example for the design of polynuclear 3d-4f materials using calixarenes which might lead to some interesting SMM properties. Our efforts to prepare isotypic compounds with other transition metals or lanthanides are ongoing.

Acknowledgements

Notes and references

1 C. Benelli and D. Gatteschi, *Chem. Rev.*, 2002, **102**, 2369–2387.
2 M. Sakamoto, K. Manseki and H. Ōkawa, *Coord. Chem. Rev.*, 2001, **219–221**, 379–414.
3 A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei and D. Gatteschi, *J. Am. Chem. Soc.*, 1985, **107**, 8128–8136.
4 A. Bencini, C. Benelli, A. Caneschi, A. Dei and D. Gatteschi, *Inorg. Chem.*, 1986, **25**, 572–575.
5 M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn and J. C. Trombe, *J. Am. Chem. Soc.*, 1993, **115**, 1822–1829; X. M. Chen, S. M. J. Aubin, Y. L. Wu, Y. S. Yang, T. C. W. Mak and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1995, **117**, 9600–9601; R. E. P. Winpenny, *Chem. Soc. Rev.*, 1998, **27**, 447–452; A. J. Stemmler, J. W. Kampf, M. L. Kirk, B. H. Atasi and V. L. Pecoraro, *Inorg. Chem.*, 1999, **38**, 2807–2817; S. C. Xiang, S. M. Hu, T. L. Sheng, R. B. Fu, X. T. Wu and X. D. Zhang, *J. Am. Chem. Soc.*, 2007, **129**, 15144–15146; K. G. Alley, A. Mukherjee, R. Clérac and C. Boskovic, *Dalton Trans.*, 2008, 59–63.
6 T. Yi, S Gao and B. Li, *Polyhedron*, 1998, **17**, 2243–2248; C. M. Zaleski, E. C. Depperman, J. W. Kampf, M. L. Kirk and V. L. Pecoraro, *Angew. Chem., Int. Ed.*, 2004, **43**, 3912–3914; Y. Kim, Y. Park and D. Y. Jung, *Dalton Trans.*, 2005, 2603–2609; B. Wu, *Dalton Trans.*, 2006, 5113–5114; T. K. Prasad, M. V. Rajasekharan and J. P. Costes, *Angew. Chem., Int. Ed.*, 2007, **46**, 2851–2854; V Chandrasekhar, B. M. Pandian, R. Boomishankar, A. Steiner and R. Clérac, *Dalton Trans.*, 2008, 5143–5145.
7 B. Zhao, P. Cheng, Y. Dai, C. Cheng, D. Z. Liao, S. P. Yan, Z. H. Jiang and G. L. Wang, *Angew. Chem., Int. Ed.*, 2003, **42**, 934–936; B. Zhao, P. Cheng, X. Y. Chen, C. Cheng, W. Shi, D. Z Liao, S. P. Yan and Z. H. Jiang, *J. Am. Chem. Soc.*, 2004, **126**, 3012–3013; B. Zhao, X. Y. Chen, P. Cheng, D. Z. Liao, S. P. Yan and Z. H. Jiang, *J. Am. Chem. Soc.*, 2004, **126**, 15394–15395; B. Zhao, H. L. Gao, X. Y. Chen, P. Cheng, W. Shi, D. Z. Liao, S. P. Yan and Z. H. Jiang, *Chem.–Eur. J.*, 2006, **12**, 149–158.
8 Y. F. Bi, Y. L. Li, W. P. Liao, H. J. Zhang and D. Q. Li, *Inorg. Chem.*, 2008, **47**, 9733–9735.
9 C. Desroches, G. Pilet, S. A. Borshch, S. Parola and D. Luneau, *Inorg. Chem.*, 2005, **44**, 9112–9120.
10 N. Morohashi, N. Iki, S. Miyano, T. Kajiwara and T. Ito, *Chem. Lett.*, 2001, 66–67.
11 N. Iki, Y. Yamane, N. Morohashi, T. Kajiwara, T. Ito and S. Miyano, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 1132–1139.
12 N. Iki, H. Kumagai, N. Morohashi, K. Ejima, M. Hasegawa, S. Miyanari and S. Miyano, *Tetrahedron Lett.*, 1998, **39**, 7559–7562.
13 T. Kajiwara, N. Iki and M. Yamashita, *Coord. Chem. Rev.*, 2007, **251**, 1734–1746.

14 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.

15 P. van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1990, **46**, 194–201.

16 N. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1991, **47**, 192–197.

17 N. Iki and S. Miyano, *J. Inclusion Phenom. Macrocyclic Chem.*, 2001, **41**, 99–105.

18 D. Gatteschi and L. Pardi, *Gazz. Chim. Ital.*, 1993, **123**, 231–240.

19 N. E. Chakov, W. Wernsdorfer, K. A. Abboud and G. Christou, *Inorg. Chem.*, 2004, **43**, 5919–5930; X. T. Wang, B. W. Wang, Z. M. Wang, W. Zhang and S. Gao, *Inorg. Chim. Acta*, 2008, **361**, 3895–3902.

20 Y. H. Wan, L. P. Zhang, L. P. Jin, S. Gao and S. Z. Lu, *Inorg. Chem.*, 2003, **42**, 4985–4994.