A One-dimensional Double-chain Compound Constructed from Ce^{III} Cations and $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ Anions: Synthesis, Crystal Structure and Magnetic Properties

Mi-Xia Hu, Ya-Guang Chen, Dong-Mei Shi, Hai-Jun Pang, and Chun-Jing Zhang

Key Laboratory of Polyoxometalates, Science of Ministry of Education, Faculty of Chemistry,
Northeast Normal University, Changchun, Jilin, 130024, P. R. China

Reprint requests to Dr. Yaguang Chen. E-mail: chenyg146@nenu.edu.cn

Z. Naturforsch. **2008**, *63b,* 968 – 972; received April 8, 2008

A polyoxometalate compound consisting of monovacant Keggin anions and trivalent lanthanide cations, $K_2H_2\{Ce(H_2O)_6[Ce(H_2O)_2(\alpha\text{-}SiW_{11}O_{39})]\}_2 \cdot 26H_2O$ (**1**), has been synthesized and characterized by elemental analysis, IR and UV spectroscopy, TG analysis, and single crystal X-ray diffraction. Compound **1** crystallizes in the triclinic system with space group $P\bar{1}$. The coordination of the monovacant Keggin anions and the Ce^{3+} ions creates a double-chain structure. The K^+ cations link the double-chains to form corrugated layers, and the layers are further connected into a 3D architecture through hydrogen bonds. A variable temperature magnetic study indicates antiferromagnetic coupling in compound **1**.

Key words: Monovacant Keggin Anions, Lanthanide Cations, Double-chain Structure, Antiferromagnetic Coupling

Introduction

Because of their wide range of topologies and a multitude of interesting properties, the polyoxometalates (POMs) have attracted increasing attention over the past decades [1, 2], and have found applications in fields like catalysis, medicine, analytical chemistry, separation science, molecular electronics, *etc.* [3 – 7]. To date, the famous Keggin anion $[XM_{12}O_{40}]^{n-}$ and its derivatives have been studied most owing to the electronic versatility and structural diversity [8]. It is well known that monovacant Keggin POMs are easily obtained by removing one WO^{4+} unit at a special pH value of their solutions [9]. These species have great ability to bind transition metal and rare-earth metal cations at their defect sites [10]. Compared with transition-metal cations, rare-earth ions with larger sizes and higher coordination numbers are suitable for linking polyoxoanions together to form new classes of structures. After Peacock and Weakley's preparation of 1 : 2 $[Ln(SiW_{11}O_{39})_2]^{13-}$ complexes [10b], the crystal structures of the 1 : 2 lanthanide α-undecatungstosilicate complexes $[Ln(\alpha\text{-}SiW_{11}O_{39})_2]^{13-}$ (Ln = Nd^{3+}, Pr^{3+}, Ce^{3+}) were reported in 1991 [11]. Pope and coworkers synthesized two one-dimensional zigzag chain-structured compounds of the type $[Ln(\alpha\text{-}SiW_{11}O_{39})_2(H_2O)_3]^{13-}$ (Ln = La^{III}, Ce^{III}) [12]. In 2003, Mialane and coworkers reported the solid state structures of 1 : 1-type $Ln[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ (Ln = Eu^{III}, Gd^{III}, Yb^{III}) and 2 : 1-type $[Nd_2(\alpha\text{-}SiW_{11}O_{39})(H_2O)_{11}]^{2-}$ complexes and found that the difference of the structures is strongly dependent on the lanthanide cations used [13]. Furthermore, $[\{Er(H_2O)_6[Er(H_2O)_3(\alpha\text{-}SiW_{11}O_{39})]\}_2]^{4-}$ [14], $[\{Sm(H_2O)_7[Sm(H_2O)_2(DMSO)(\alpha\text{-}SiW_{11}O_{39})]\}]^{2-}$ [15] and $[Ln_2(\alpha\text{-}SiW_{11}O_{39})(H_2O)_{11}]^{2-}$ (Ln = Ce, La) [16] exhibit structures analogous to $[Nd_2(\alpha\text{-}SiW_{11}O_{39})(H_2O)_{11}]^{2-}$ [13]. A 1D infinite chain-like structure $[(Pr(H_2O)_4SiW_{11}O_{39})(NaPr_2(H_2O)_{12})(Pr(H_2O)_4SiW_{11}O_{39})]^{3-}$ [17] and dimeric $K_{12}[(SiW_{11}O_{39}Ln)_2(\mu\text{-}CH_3COO)_2]$ (Ln = Gd^{III}, Yb^{III}) [18] complexes have also been reported. All the above studies indicate the combinatorial diversity between the lanthanide cations and the monovacant Keggin-type polyanions. Therefore, to explore new combination modes of monovacant Keggin-type POMs and Ln^{III} ions is a very interesting challenge. Herein, the synthesis, thermogravimetric analysis, spectroscopic, variable-temperature magnetic and structural characterization of the compound $K_2H_2\{Ce(H_2O)_6[Ce(H_2O)_2(\alpha\text{-}SiW_{11}O_{39})]\}_2 \cdot 26H_2O$ (**1**) are reported. To the best of our knowledge, this is the first example of a one-dimensional double-chain structure constructed from monovacant POMs and lanthanide cations.

Results and Discussion

The asymmetrical unit of **1** consists of one anion $[Ce_2(H_2O)_8(\alpha\text{-}SiW_{11}O_{39})]^{2-}$ (Fig. 1), one K^+ cation, and a large number of water molecules. In the two crystallographically unique cations, Ce(1) resides in the vacant site of the $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ anion (d(Ce–O) 2.427(16) – 2.474(16) Å), and is additionally coordinated by two adjacent $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ anions *via* terminal oxygen atoms (O24 and O25) (d(Ce–O_d) 2.481(16) and 2.561(16) Å). Note that the linkage of $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ anions and $Ce(1)^{3+}$ cations leads to a zigzag chain directed along the a axis, which is similar to the structure of $[Ce(\alpha\text{-}SiW_{11}O_{39})(H_2O)_3]^{5-}$ [12], $[Eu(\alpha\text{-}SiW_{11}O_{39})(H_2O)_2]^{5-}$ [13] and $[Eu(H_2O)_4PW_{11}O_{39}]^{4-}$ [19]. However, the Ce (1) cation is coordinated by two water molecules (d(Ce–OH_2) 2.543(17) and 2.568(17) Å) rather than three water molecules, which is different from the coordination in $[Ce(\alpha\text{-}SiW_{11}O_{39})(H_2O)_3]^{5-}$ [12]. The eight oxygen atoms coordinated to the Ce(1) cation form a bicapped trigonal prism (Fig. 2), which is one of the common coordination arrangements for complexes with a coordination number of 8 [20, 21]. The groups of O14, O21, O40 and O8, O11, O17 form the two trigonal planes, while the two terminal oxygen atoms (O24, O25) from the $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ anions occupy the cap sites.

The Ce(2) cation is coordinated to the $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ anions *via* terminal oxygen atoms (O18, O41) with Ce–O_d distances of 2.562(17) and 2.495(18) Å, forming the A and B chains on the two sides of the zigzag chain. As a result, compound **1** displays a novel one-dimensional double-chain structure (Fig. 3). In addition to two terminal oxygen atoms of the two $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ anions, the coordination environment of the Ce(2) cation center is completed by six water molecules (d(Ce–OH_2) 2.52(2) – 2.746(19) Å). The coordination sphere of the eight-coordinate Ce(2) cation displays a distorted tricapped trigonal prism configuration. The groups of O2w, O9w, O41 and O1w, O6w, O7w form the two trigonal planes, and O18 and O8w occupy the cap sites.

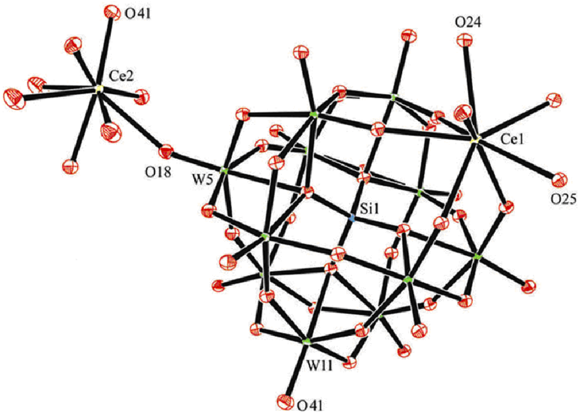

Fig. 1. ORTEP drawing of **1** with displacement ellipsoids at the 50 % probability level.

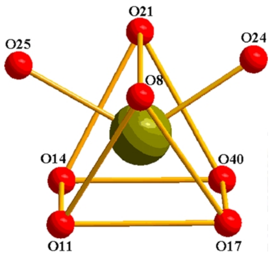

Fig. 2. Coordination polyhedron around Ce(1) in **1**. Hydrogen atoms are omitted for clarity.

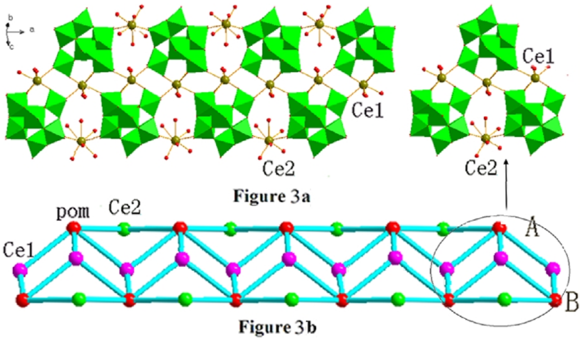

Fig. 3. a) Polyhedral representation of **1** showing the double-chain structure. All the hydrogen atoms and water molecules have been omitted for clarity; b) Schematic view of the double-chain structure.

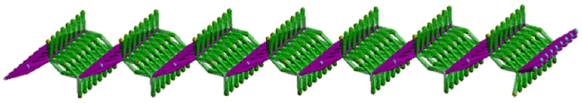

Fig. 4. Schematic view of a corrugated layer in **1** (the green sticks symbolize the links between Ce and SiW_{11} clusters, and the purple sticks symbolize the links between K and SiW_{11} clusters; color online).

K^+ cations link the double-chains to form an infinite corrugated layer structure (Fig. 4). The coordination sphere of the K^+ cation is defined by two terminal oxygen atoms (O13 and O30) and one bridging oxygen atom (O35) from the $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ anion of a double-chain, two terminal oxygen atoms (O15

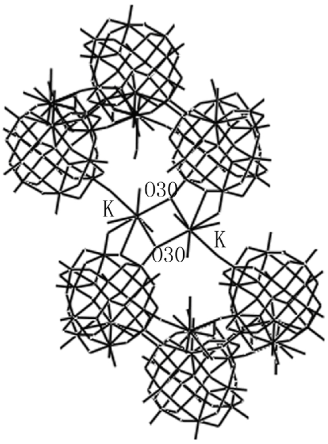

Fig. 5. The coordination environment of the potassium ions.

and O30) from two adjacent [α-$SiW_{11}O_{39}$]$^{8-}$ anions of another double-chain, and three water molecules (d(K–O) 2.73(2) – 3.095(18) Å). Because of the presence of an inversion center, there are two such K^+ cations which results in a double K-bridging. This is similar to the location of the Na1 atom in $Na_5[(A\text{-}\alpha\text{-}SiW_9O_{33}H_3)_2\,K\{UO_2(H_2O)\}_2]$ reported by our group [22] (Fig. 5). Both K^+ cations share the same terminal oxygen atom (O30) of the [α-$SiW_{11}O_{39}$]$^{8-}$ anions.

Due to the existence of coordinated and interstitial water molecules, there are multifold hydrogen bonds between the layers with O$\cdots$O distances in the range of 2.514 – 3.035 Å to form a three-dimensional architecture.

FT-IR spectrum

The IR spectrum of **1** shows that the POM anions are in the basic Keggin structure. The characteristic peaks at 954, 883, 819, and 683 cm^{-1} are attributed to ν_{as}(W=O_d), ν_{as}(Si–O_a), ν_{as}(W–O_b–W), and ν_{as}(W–O_c–W), respectively. Compared to α-$K_8SiW_{11}O_{39}\cdot 13H_2O$ [23], the IR spectrum indicates that the polyoxoanions in compound **1** are slightly distorted due to the incorporation of Ce^{III} ions. The strong peak at 1620 cm^{-1} is assigned to the deformation vibrations of interstitial and coordinated water molecules.

UV spectrum

The UV spectrum of **1** in aqueous solution shows three absorption bands at approximately 195, 222 and 251 nm. The absorption at 195 nm is attributed to the $O_d \rightarrow$ W charge transfer. The absorptions at 222 and 251 nm can be ascribed to $f \rightarrow f$ transitions of Ce^{III} consistent with reference [24]. The absorption of $O_{b/c} \rightarrow$ W (expected at *ca.* 250 – 270 nm) [25] might be overlapped by this band.

TG analysis

The TG curve of **1** in the temperature range of 30 – 600 ℃ shows a total weight loss of 11.5 % which is in good agreement with the calculated value of 11.2 %, corresponding to the removal of all water molecules. The sample weight was unchanged at temperatures higher than 552 ℃.

Magnetic properties

The variable-temperature magnetic susceptibility of **1** was studied in the temperature range of 2 – 300 K. The experimental data plotted as χ_m *versus* T are shown in Fig. 6, the $\chi_m T$ *vs.* T curve given as an inset. As the temperature decreases, the χ_m value increases from 0.015 cm^3 mol^{-1} at 300 K to a maximum of 0.79 cm^3 mol^{-1} at about 2 K. The experimental $\chi_m T$ value steadily decreases upon cooling from 4.38 emu K mol^{-1} at 300 K to 1.58 emu K mol^{-1} at about 2 K. At r. t., the comparison of the measured value μ_{eff} = 5.80 μ_B to the spin-only calculated value (3.48 μ_B) suggests the contribution of an orbit magnetic moment. In the temperature range of 94 – 295 K, the magnetic susceptibility of **1** follows the Curie-Weiss law, $\chi_m = C/(T-\theta)$ with a Curie constant C = 5.23 emu K mol^{-1} and a Weiss constant $\theta = -78.4$ K. The result indicates the occurrence of antiferromagnetic coupling. According to the crystal structure of **1**, it can be assumed that the antiferromagnetic behavior

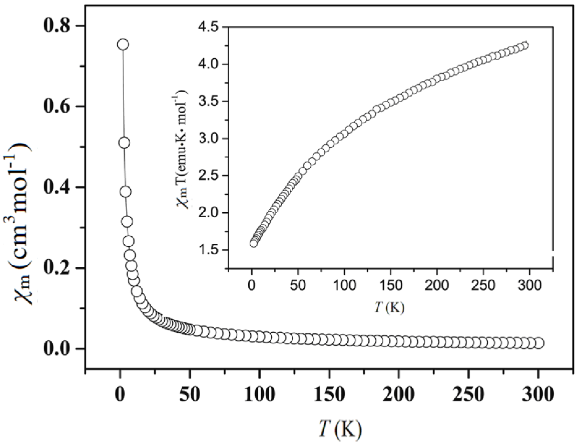

Fig. 6. Temperature dependence of χ_m and $\chi_m T$ (inset) for **1**.

of **1** may be due to superexchange interactions between the Ce(2) ions through the WO_6 octahedra [26]. As the temperature decreases from 94 to 2 K, the deviation from the Curie-Weiss law of the magnetic susceptibility indicates the presence of strong spin-orbit coupling interactions and a crystal field effect at low temperature.

Conclusions

In summary, a new complex **1** has been synthesized and structurally characterized. Because of the different coordination of the Ce^{III} cations with $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ anions, a novel one-dimensional double-chain structure is constructed. The magnetic studies of compound **1** demonstrate an anti-ferromagnetic superexchange interaction between the Ce(2) ions. In future work, we will explore if other lanthanides can form an analogous structure or if novel Keggin polyoxoanion-based extended structures can be realized by adding appropriate ligands.

Experimental Section

General procedures

All reagents were purchased and used without further purification. $\alpha\text{-}H_4SiW_{12}O_{40}$ was synthesized according to published procedures [23] and identified by its IR spectrum. Elemental analyses (W, Ce, K) were carried out with a Leaman inductively coupled plasma (ICP) spectrometer. The IR spectrum with KBr pellets was obtained on an Alpha Centaur FT/IR spectrometer in the 400 – 4000 cm^{-1} region. The UV spectrum was recorded on a 756 CRT UV/Vis spectrophotometer. TG analysis was performed on a Perkin-Elmer TGA7 instrument in an atmosphere of N_2 with a heating rate of 10 °C min^{-1}. The variable temperature magnetic susceptibility measurements for **1** were carried out on a Quantum Design MPMS-5SQUID magnetometer with an applied field of 1000 Oe. A diamagnetic correction was estimated from Pascal's constants.

Synthesis of $K_2H_2\{Ce(H_2O)_6[Ce(H_2O)_2(\alpha\text{-}SiW_{11}O_{39})]\}_2 \cdot 26H_2O$ *(1)*

$Ce(NO_3)_3 \cdot 6H_2O$ (0.1102 g, 0.26 mmol) was dissolved in 15 mL of water, and the solution was heated to about 80 °C. A solution (10 mL) containing $\alpha\text{-}H_4SiW_{12}O_{40}$ (0.39 g, 0.13 mmol) was added, and the mixture was stirred for 15 min. The pH value of the resulting solution was adjusted to 6.23 with KOH (1 mol · L^{-1}), and then the solution was stirred for *ca.* 1 h. Cooled to r. t., the solution was filtered and concentrated under ambient conditions. After 27 d, yellow crystals suitable for X-ray diffraction were obtained (31 % yield, based on Ce). Elemental analysis: calcd. W 59.95, Ce 8.31, K 1.18; found W 58.86, Ce 7.96, K 1.03. – IR (solid KBr pellet): ν = 1620(s), 1003 (m), 954 (m), 883 (m), 819 (w), 686 (m), 524(m) cm^{-1}.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$H_{86}Ce_4K_2O_{120}Si_2W_{22}$
Formula weight	6746.24
Color, habit	yellow, block
Cryst. size, mm^3	$0.12 \times 0.11 \times 0.10$
Temperature, K	293(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	11.707(5)
b, Å	12.449(5)
c, Å	18.128(5)
α, deg	77.132(5)
β, deg	83.589(5)
γ, deg	86.316(5)
V, $Å^3$	2557.4(17)
Z	1
D_{calc}, g cm^{-3}	4.38
$F(000)$, e	2972
hkl range	$-13 \le h \le 14$, $-15 \le k \le 14$, $-20 \le l \le 22$
Radiation; λ, Å	MoK_α; 0.71073
Absorption coefficient, mm^{-1}	26.6
Absorption correction	empirical
θ range for data collection, deg	1.68 – 25.75
Measured reflections	13596
Independent reflections, R_{int}	9572, 0.03
Completeness,%	97.7
Observed reflections	7002
Data / ref. parameters	9572 / 673
Maximun shift/error	0.000
Extinction coefficient	0.00015(3)
GOF on F^2	1.131
Final $R1$, $wR2$ [$I \ge 2\sigma(I)$]	0.057, 0.164
Final $R1$, $wR2$ (all data)	0.086, 0.177
Largest diff. peak / hole, e $Å^{-3}$	3.19 / −7.85

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \Sigma[w(F_o{}^2 - F_c{}^2)^2] \,/\, \Sigma[w(F_o{}^2)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) for **1**.

Ce(1)–O(17)	2.427(16)	Ce(1)–O(24)$^{\#3}$	2.481(16)
Ce(1)–O(11)	2.438(16)	Ce(1)–O(8)	2.543(17)
Ce(1)–O(14)	2.453(16)	Ce(1)–O(25)$^{\#4}$	2.561(16)
Ce(1)–O(40)	2.474(16)	Ce(1)–O(21)	2.568(17)
Ce(2)–O(41)	2.495(18)	Ce(2)–O(18)	2.562(17)
Ce(2)–O(6W)	2.52(2)	Ce(2)–O(2W)	2.585(19)
Ce(2)–O(8W)	2.54(2)	Ce(2)–O(7W)	2.63(2)
Ce(2)–O(1W)	2.55(2)	Ce(2)–O(9W)	2.746(19)

Symmetry transformations used to generate equivalent atoms: $^{\#3}$ $-x+1$, $-y$, $-z+1$; $^{\#4}$ $-x$, $-y$, $-z+1$.

X-Ray crystallography

The data were collected on a Bruker Smart CCD diffractometer with graphite-monochromated MoK_α radiation at 293 K. An empirical absorption correction was applied.

The structure was solved by Direct Methods using the program SHELXS-97 and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [27]. All non-hydrogen atoms were refined anisotropically. A summary of the crystallographic data and structure determination is listed in Table 1, and selected bond lengths are presented in Table 2. The appearance of a peak of -7.85 e Å^{-3} 0.6 Å away from Ce(2) is attributed to series termination errors.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-418602.

Acknowledgements

This work was supported by the Analysis and Testing Foundation of the Northeast Normal University. We thank Prof. Zhong-ming Su's research group for the X-ray diffraction data collection.

---

[1] a) D. B. Mitzi, *Chem. Mater* **2001**, *13*, 3283 – 3298; b) D. B. Mitzi, *Prog. Inorg. Chem.* **1999**, *48*, 1 – 121.

[2] a) M. Yagi, K. Sone, M. Yamada, S. Umemiya, *Chem. Eur. J.* **2005**, *11*, 767 – 775; b) D. L. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.* **2007**, *36*, 105 – 121.

[3] M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin **1983**.

[4] M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56 – 70; *Angew. Chem. Int. Ed.* **1991**, *30*, 34 – 48.

[5] P. Gouzerh, A. Proust, *Chem. Rev.* **1998**, *98*, 77 – 111.

[6] R. C. Howell, F. G. Perez, S. Jain, W. D. Horrocks, Jr., A. L. Rheingold, L. C. Francessconi, *Angew. Chem.* **2001**, *113*, 4155 – 4158; *Angew. Chem. Int. Ed.* **2001**, *40*, 4031 – 4034.

[7] X. B. Cui, J. Q. Xu, Y. Li, Y. H. Sun, G. Y. Yang, *Eur. J. Inorg. Chem.* **2004**, 1051 – 1055.

[8] C. L. Hill (Ed.), *Chem. Rev.* **1998**, *98*, 1 – 387.

[9] L. C. W. Baker, V. E. S. Baker, K. Eriks, M. T. Pope, M. Shibata, O. W. Rollins, J. H. Fang, L. L. Koh, *J. Am. Soc. Chem.* **1966**, *88*, 2329 – 2331.

[10] a) L. C. W. Baker, V. E. S. Baker, *J. Inorg. Nucl. Chem.* **1967**, *29*, 2935 – 2944; b) R. D. Peacock, T. J. R. Weakley, *J. Chem. Soc. A* **1971**, 1836 – 1839.

[11] a) Y. K. Shan, Z. X. Liu, *Sci. China, Ser. B* **1991**, *34*, 313; b) Y. K. Shan, Z. X. Liu, *Acta Chim. Sin.* **1992**, *50*, 357 – 364; c) R. Q. Sun, H. H. Zhang, S. L. Zhao, C. C. Huang, X. L. Zheng, *Chin. J. Struct. Chem.* **2001**, *20*, 413 – 417.

[12] M. Sadakane, M. H. Dickman, M. T. Pope, *Angew. Chem.* **2000**, *112*, 3036 – 3038; *Angew. Chem. Int. Ed.* **2000**, *39*, 2914 – 2916.

[13] P. Mialane, L. Lisnard, A. Mallard, J. Marrot, E. Antic-Fidancev, P. Aschehoug, D. Vivien, F. Secheresse, *Inorg. Chem.* **2003**, *42*, 2102 – 2108.

[14] J. Y. Niu, J. W. Zhao, J. P. Wang, *J. Mol. Struct.* **2004**, *701*, 19 – 24.

[15] J. P. Wang, J. W. Zhao, X. Y. Duan, J. Y. Niu, *Cryst. Growth Des.* **2006**, *6*, 507 – 513.

[16] F. Y. Li, Y. G. Wei, G. G. Gao, L. F. Fan, Z. K. Li, *Inorg. Chim. Acta* **2006**, *359*, 3795 – 3799.

[17] J. Y. Niu, J. W, Zhao, J. P. Wang, *Inorg. Chem. Commun.* **2004**, *7*, 876 – 879.

[18] P. Mialane, A. Dolbecq, E. Rivière, J. Marrot, F. Sécheresse, *Eur. J. Inorg. Chem.* **2004**, 33 – 36.

[19] C. Zhang, R. C. Howell, K. B. Scotland, F. G. Perez, L. Todaro, L. C. Francesconi, *Inorg. Chem.* **2004**, *43*, 7691 – 7701.

[20] C. Lescop, E. Belorizky, D. Luneau, P. Rey, *Inorg. Chem.* **2002**, *41*, 3375 – 3384.

[21] J. Y. Niu, M. L. Wei, J. P. Wang, D. B. Dang, *Eur. J. Inorg. Chem.* **2004**, 160 – 170.

[22] Y. G. Chen, F. X. Meng, H. J. Pang, Y. Sun, *J. Cluster Sci.* **2007**, *18*, 396 – 405.

[23] A. Teze, G. Herve, *Inorg. Synth.* **1990**, *27*, 85 – 96.

[24] Q. Su, *Chemistry of Rare Earths* (Henan Science and Technology Publication), Zhengzhou **1993**.

[25] J. Y. Niu, J. P. Wang, *Introduction of Heteropoly Compounds*, Henan University Press, Kaifeng, P. R. China, **2000**, p. 189.

[26] J. Lu, E. Shen, M. Yuan, Y. Li, E. Wang, C. Hu, L. Xu, J. Peng, *Inorg. Chem.* **2003**, *42*, 6956 – 6958.

[27] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**.