J. Braz. Chem. Soc., Vol. 17, No. 7, 1355-1359, 2006.
Printed in Brazil - ©2006 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Synthesis, Crystal Structure and Thermal Decomposition Mechanism of a Samarium *o*-Chlorobenzoate Complex with 1,10-Phenanthroline

Jian-Jun Zhang,[*,a] Ning Ren,[a,b] Yan-Xun Wang,[c] Su-Ling Xu,[a,b] Rui-Fen Wang[b] and Shu-Ping Wang[b]*

[a]*Experimental Center, Hebei Normal University, Shijiazhuang, 050016, P. R.China*

[b]*College of Chemistry & Material Science, Hebei Normal University, Shijiazhuang, 050016, P. R. China*

[c]*Hebei Institute of Architectural and Civil Engineering, Zhangjiakou, 075024, P. R. China*

O complexo [Sm(o–ClBA)$_3$phen]$_2$ (o–ClBA= o-clorobenzoato; phen= 1,10-fenantrolina) foi preparado pela reação de $SmCl_3 \cdot 6H_2O$ com ácido o-clorobenzóico e 1,10-fenantrolina. O complexo foi caracterizado por um estudo de difração de raios-X, análise elementar, espectroscopia no infravermelho e técnicas TG-DTG. O cristal é triclínico, grupo espacial $P\bar{1}$ com a = 13,157(3) Å, b = 14,139(4) Å, c = 17,397(4) Å, α = 83,755(3)º, β = 84,064(3)º, γ = 73,434(3)º, Z=2, Dc=1,722 Mg/m^3, F(000)=1572. Contém duas unidades cristalograficamente distintas de $Sm(o\text{-}ClC_6H_4COO)_3(C_{12}H_8N_2)$, formando dois tipos de moléculas binucleares. Cada Sm^{3+} encontra-se coordenado a dois átomos de oxigênio de um grupo carboxilato bidentado quelante, cinco átomos de oxigênio de dois grupos carboxilatos bidentados ligados em ponte e de três grupos carboxilatos tridentados quelantes e ligados em ponte, e a dois átomos de nitrogênio de uma molécula de 1,10-fenantrolina, completando uma geometria monoencampuzada antiprismática quadrada. A decomposição térmica deste composto foi estudada por técnicas TG-DTG, e os parâmetros cinéticos da primeira etapa da decomposição foram determinados pelos métodos de Kissinger e Ozawa-Doyle. A equação de meia vida após 10% de perda de peso, $\ln\tau = -26{,}8166+20319{,}94/T$, foi deduzida por análise termogravimétrica da isoterma.

The title complex [Sm(o–ClBA)$_3$phen]$_2$ (o–ClBA= o-chlorobenzoate; phen= 1,10-phenanthroline) was prepared by the reaction of $SmCl_3 \cdot 6H_2O$, o-chlorobenzoic acid and 1,10-phenanthroline. The complex was characterized by single crystal X-ray diffraction, elemental analysis, IR spectra and TG-DTG techniques. The results show that the crystal is triclinic, space group $P\bar{1}$ with a = 13.157(3) Å, b = 14.139(4) Å, c = 17.397(4) Å, α = 83.755(3)º, β = 84.064(3)º, γ =73.434(3)º, Z=2, Dc=1.722 Mg/m^3, F(000)=1572. The crystal contains two crystallographically distinct $Sm(o\text{-}ClC_6H_4COO)_3(C_{12}H_8N_2)$ units, forming two types of binuclear molecule. Each Sm^{3+} is coordinated to two O atoms of one bidentate chelating carboxylate group, five O atoms of two bidentate bridging and two tridentate chelating-bridging carboxylate groups, and two N atoms of one 1,10-phenanthroline molecule to complete a distorted mono-capped square antiprism geometry. Its thermal decomposition mechanism was determined by TG-DTG techniques, and kinetic parameters have been studied on the first-step decomposition of [Sm(o–ClBA)$_3$phen]$_2$ by means of Kissinger's method and Ozawa-Doyle's method. The lifetime equation at weight-loss of 10% was deduced as $\ln\tau = -26.8166+20319.94/T$ by isothermal thermogravimetric analysis.

Keywords: *o*-chlorobenzoic acid, crystal structure, 1,10-phenanthroline, samarium complex, thermal decomposition kinetics

Introduction

The coordination chemistry of rare-earth cations with various carboxylic acids has become increasingly significant in the recent years, due to the potential applications in many areas, such as extraction, separation, germicide preparation, catalysis, luminescence and functional material preparation.[1] Perhaps, the most important feature of the rare-earth carboxylate complexes is the large number of coordination types exhibited by these ligands, e.g, bidentate chelating, bidentate bridging or tridentate chelating-bridging.[2] For this reason there has been continuing interest in the study of such complexes. In previous work,[3-15] we reported the synthesis, crystal structure and thermal

---

*e-mail: jjzhang6@sohu.com

decomposition behavior of a number of europium or terbium complexes with benzoic acid or its derivatives and 1,10-phenanthroline. In this work, we describe the synthesis and crystal structure, of the title complex, determined by a single crystal X-ray diffraction study. We also discuss a mechanism for the thermal decomposition, studied by TG-DTG techniques, from which we obtained the activation energy *E* and the pre-exponential factor *A* using Kissinger's method[16] and Ozawa-Doyle's method.[17-18]

Results and Discussion

Infrared spectra

The free acid COOH group band at 1693 cm^{-1}, completely disappears in the spectra of the complex. However, the bands arising from asymmetric and symmetric vibrations of the COO$^-$ group occur at 1591 cm^{-1}, 1545 cm^{-1}, 1519 cm^{-1} and 1477 cm^{-1}, 1403 cm^{-1}, 1350 cm^{-1}, respectively. This indicated that the carboxyl groups are bonded to Sm(III) ion in three coordination modes,[19] which was confirmed by X-ray diffraction analysis. In addition, the bands of $\nu_{C=N}$ (1646 cm^{-1}) and $\delta_{C\text{-}H}$ (854cm^{-1}, 740cm^{-1}) attributed to 1,10-phenanthroline are observed to move lower wave numbers at 1617 cm^{-1}, 852 cm^{-1} and 730 cm^{-1}, respectively. This indicated that the Sm^{3+} ions were coordinated by the nitrogen atoms of the 1,10-phenanthroline.[20]

Table 1. Crystallographic data and structure refinement for [Sm(*o*–ClBA)$_3$phen]$_2$

Empirical formula	$C_{66}H_{40}Cl_6N_4O_{12}Sm_2$
Formula weight	1594.42
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, *P* ī
Unit cell dimensions	a = 13.157(3) Å α = 83.755(3)º b = 14.139(4) Å β = 84.064(3)º c = 17.397(4) Å γ = 73.434(3)º
Volume	3074.8(13) Å^3
Z, Calculated density	2, 1.722 Mg m^{-3}
Absorption coefficient	2.219 mm^{-1}
F(000)	1572
Crystal size	0.38 × 0.30 × 0.22 mm
Theta range for data collection	1.84 to 25.03º
Limiting indices	-15≤h≤15, -16≤k≤16, -20≤l≤12
Reflections collected / unique	16702 / 10701 [$R_{(int)}$ = 0.0172]
Completeness to θ = 25.03	98.4%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.648886
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10701 / 2 / 820
Goodness-of-fit on F^2	1.091
Final *R* indices [I>2σ(I)]	*R*1 = 0.0326, *wR*2 = 0.0901
R indices (all data)	*R*1 = 0.0454, *wR*2 = 0.0958
Largest diff. peak and hole	0.906 and -0.731 e. Å^{-3}

Crystal structure

Selected bond lengths and angles are listed in Table 2. The crystal is composed of two types of binuclear molecules, which are identical in composition with similar structures, as shown in Figure 1(a) and (b). In each binuclear molecule, two Sm(o-ClC$_6$H$_4$COO)$_3$(C$_{12}$H$_8$N$_2$) units are combined through crystallographic inversion center. Each Sm^{3+} ion is coordinated to nine atoms, of which five atoms are from the bidentate bridging and tridentate chelating-bridging carboxylate groups, two oxygen atoms are from bidentate chelating carboxylate groups and two nitrogen atoms are from a 1,10-phenanthroline molecule. The coordination polyhedron of Sm(III) ion adopts a distorted mono-capped square antiprism geometry. The oxygen atom from the tridentate chelating-bridging carboxylate group is at the capped position. The Sm–Sm distance in the molecule (a)(4.047

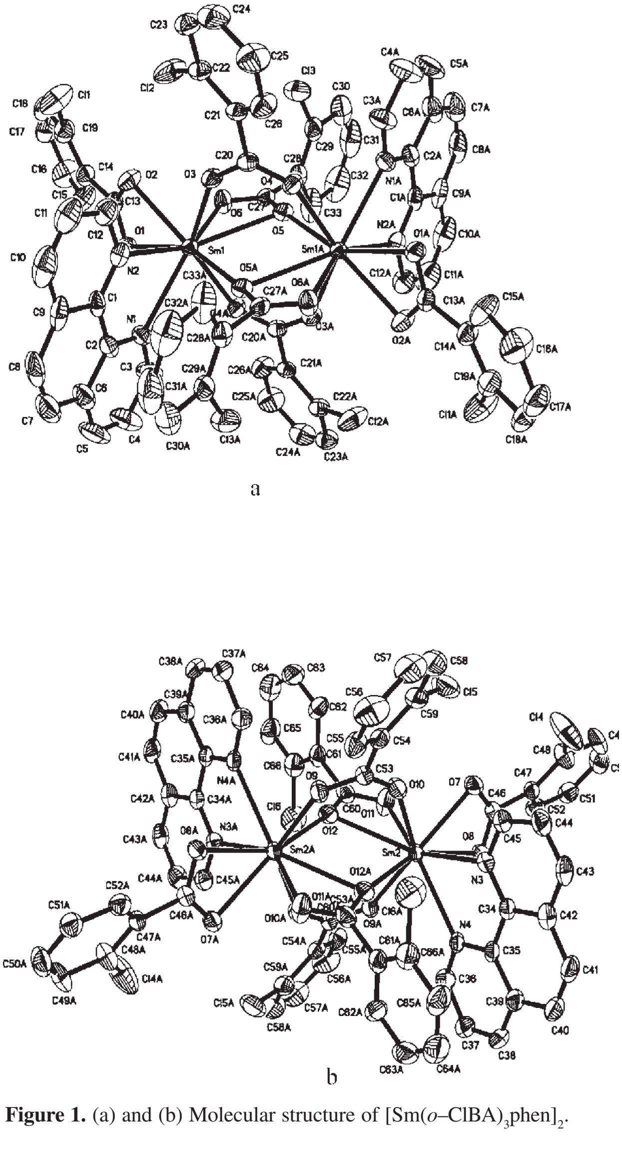

Figure 1. (a) and (b) Molecular structure of [Sm(*o*–ClBA)$_3$phen]$_2$.

Table 2. Selected bond lengths (Å) and angles (°) for the molecules (a) and (b)

Sm1-O3	2.350(3)	Sm2-O12[a]	2.345(3)
Sm1-O5[a]	2.379(3)	Sm2-O10	2.377(4)
Sm1-O4[a]	2.395(3)	Sm2-O9[a]	2.381(4)
Sm1-O2	2.433(4)	Sm2-O8	2.439(4)
Sm1-O6	2.479(4)	Sm2-O11	2.482(4)
Sm1-O1	2.487(3)	Sm2-O7	2.484(4)
Sm1-N2	2.598(5)	Sm2-N3	2.604(4)
Sm1-N1	2.609(4)	Sm2-N4	2.675(4)
Sm1-O5	2.728(4)	Sm2-O12	2.695(4)
Sm1-Sm1[a]	4.047(9)	Sm2-Sm2[b]	4.016(10)
O3-Sm1-O5[a]	74.06(12)	O12[b] -Sm2-O10	73.25(13)
O3-Sm1-O4[a]	133.62(12)	O12[b] -Sm2-O9[b]	77.06(12)
O5[a] -Sm1-O4[a]	76.71(12)	O10-Sm2-O9[b]	134.56(12)
O3-Sm1-O2	75.85(12)	O12[b] -Sm2-O8	152.30(13)
O5[a]-Sm1-O2	144.77(12)	O10-Sm2-O8	127.13(12)
O4[a] -Sm1-O2	138.39(13)	O9[b] -Sm2-O8	93.90(12)
O3-Sm1-O6	92.09(14)	O12[b] -Sm2-O11	123.16(13)
O5[a] -Sm1-O6	123.80(12)	O10-Sm2-O11	91.38(17)
O4[a] -Sm1-O6	75.38(14)	O9[b] -Sm2-O11	76.99(16)
O2-Sm1-O6	74.92(14)	O8-Sm2-O11	78.76(14)
O3-Sm1-O1	128.04(12)	O12[b] -Sm2-O(7)	145.08(13)
O5[a] -Sm1-O1	154.56(12)	O10-Sm2-O7	74.86(13)
O4[a] -Sm1-O1	91.17(12)	O9[b] -Sm2-O7	137.13(13)
O2-Sm1-O1	52.34(12)	O8-Sm2-O7	52.67(12)
O6-Sm1-O1	72.79(12)	O11-Sm2-O7	71.16(14)
O3-Sm1-N2	75.88(15)	O12[b]-Sm2-N3	84.27(13)
O5[a] -Sm1-N2	80.46(13)	O10-Sm2-N3	75.02(14)
O4[a] -Sm1-N2	132.90(15)	O9[b] -Sm2-N3	134.98(14)
O2-Sm1-N2	74.78(15)	O8-Sm2-N3	84.06(14)
O6-Sm1-N2	149.31(14)	O11-Sm2-N3	144.91(15)
O1-Sm1-N2	92.33(14)	O7-Sm2-N3	74.06(14)
O3-Sm1-N1	133.62(14)	O12[b] -Sm2-N4	77.42(13)
O5[a] -Sm1-N1	80.18(12)	O10-Sm2-N4	129.74(14)
O4[a] -Sm1-N1	73.66(14)	O9[b] -Sm2-N4	73.92(13)
O2-Sm1-N1	108.79(14)	O8-Sm2-N4	74.92(13)
O6-Sm1-N1	134.18(14)	O11-Sm2-N4	138.87(16)
O1-Sm1-N1	74.93(13)	O7-Sm2-N4	113.88(12)
N2-Sm1-N1	62.12(15)	N3-Sm2-N4	62.09(14)
O3-Sm1-O5	68.52(12)	O12[b] -Sm2-O12	74.57(13)

[a]-x+1,-y+2,-z+1, [b]-x+2,-y+1,-z.

Å) is longer than that in (b)(4.016 Å). In the binuclear molecule (a), the Sm–O distance is in a range of 2.350(3)–2.487(3) Å. The mean distance is 2.421Å. The average of Sm–N bond is 2.604 Å. In the binuclear molecule (b), the Sm–O bond length is in a range of 2.345(3) –2.484(4) Å, with an average of 2.418 Å. The mean bond length of Sm–N is 2.639 Å. The structure of this compound is similar to that of the analogous complex [Sm(*o*-MBA)$_3$phen]$_2$(*o*-MBA= *o*-methylbenzoate),[13] in that they both consist of two similar types of binuclear molecules. However the average Sm–O and Sm–N distances in the later complex are slightly longer than those in [Sm(*o*-ClBA)$_3$phen]$_2$. The reason may be that the methyl is electron-donation group, while the chlorin is electron-withdraw group, which result in the enhancement of electron cloud density and the strength of the chemical bond.

In both binuclear molecules (a) and (b), the Sm–O bond distances of the chelating carboxylate are longer than those of the bridging carboxylates groups, which clearly shows that the coordination of Sm^{3+} ion with the chelating carboxylate is weaker than that of Sm^{3+} ion with the bridging carboxylates groups, or rather that the formation of four-membered chelate ring with Sm^{3+} ion is unstable.[21]

Thermal decomposition mechanism

The TG-DTG curves of the title complex at a heating rate of 5 °C min^{-1} under a nitrogen atmosphere are shown in Figure 2. The DTG curve reveals three decomposition stages. The first stage starts at 279.55 °C and completes at 428.62 °C with a loss of 22.16% (theoretical loss is 22.60%), corresponding to the remove of 2 mol phen. The bond distance of the structure of the complex can demonstrate the degradation. Average bond length of Sm–N is longer than that of Sm–O, theoretically, Sm–N bond is less stable and easy to be broken down. The IR spectra of the residue at 428.62 °C also shows the disappearance of the absorption band of C=N at 1617 cm^{-1}.

The loss of the *o*-chlorobenzoate ligands occurs from 428.62 to 888.50 °C in two steps. The total weight loss is 54.80% (theoretical loss is 55.50%). Up to 888.50 °C, the title complex was completely degraded into Sm$_2$O$_3$(observed, 22.09%; calculated, 21.87%), which was demonstrated by the IR spectra of the residue at 888.50 °C. The bands of $\nu_{as(COO)}$ (1580 – 1546 cm^{-1}) and $\nu_{s(COO)}$ (1479 – 1408cm^{-1}) disappeared, and the IR spectra of the residue were same to standard spectra of Sm$_2$O$_3$.

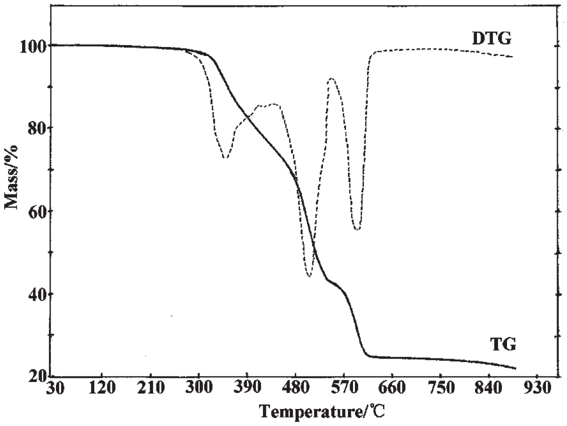

Figure 2. TG-DTG curves of [Sm(*o*–ClBA)$_3$phen]$_2$ (β=5 °C min^{-1}).

Kinetic parameters of [Sm(o–ClBA)$_3$phen]$_2$

The kinetic parameters for the first-step thermal decomposition of [Sm(*o*–ClBA)$_3$phen]$_2$ could be determined by using Kissinger's method[16] and Ozawa-

Doyle's method.[17,18] The calculated results are listed in Table 3, which are consistent with each other.

Therefore, the Arrhenius equation can be expressed with the average of E and ln A for the first-step decomposition as follows: $\ln k = 39.26–229.1\times10^3/ RT$.

Lifetime

The general lifetime formula of materials is,[10]

$$\ln\tau = a + b/T \qquad (1)$$

where τ is the lifetime at temperature T(K), a and b are constants. In this paper, the mass-loss of 10% lifetime was measured by isothermal temperature TG at 563.15, 573.15, 583.15 and 593.15 K and listed in Table 4. By substituting the values in Table 4 into equation (1), the constants a, b and linear correlation coefficients r were obtained by the linear least squares method. The lifetime equation is $\ln\tau = –26.8166+20319.94/T$. Linear correlation coefficient r is 0.9967.

Experimental

Materials

All reagents used were Analar grade and were used without further purification.

Preparation of complex [Sm(o–ClBA)$_3$phen]$_2$

$SmCl_3·6H_2O$ was obtained from the reaction of Sm_2O_3 (99.95%) and HCl (6.0 mol L^{-1}). A stoichiometric amount of *o*-chlorobenzoic acid and a quantitative amount 1,10-phenanthroline were mixed and then dissolved in 95% ethanol solution. The pH value of the mixture was adjusted to 6-7 by adding 1.0 mol L^{-1} NaOH solution, and then added dropwise to the ethanolic $SmCl_3$ solution, while a white precipitate formed. The solution mixture was stirred for 8h at room temperature and then deposited for a day. The precipitate was filtered out and washed with deionized water and 95% ethanol. Yield: 89%. Colorless cubic crystals for X-ray diffraction analysis were obtained by the slow evaporation of the filtrate. IR (KBr) ν_{max} /cm^{-1}: 1646,1617,1591,1545,1519,1477,1403, 1350 cm^{-1}. Anal. Calc. for $C_{66}H_{40}Cl_6N_4O_{12}Sm_2$: C, 49.66; H, 2.88; N, 3.51; Sm, 18.86; found C, 49.53; H, 2.36; N, 4.06; Sm, 18.81.

Table 3. Kinetic parameters for first-step thermal decomposition of [Sm(*o*–ClBA)$_3$phen]$_2$

Method	E / (kJ mol^{-1})	$\bar{E}$ / (kJ mol^{-1})	ln$A$	r
Kissinger	229.80	229.1	39.26	0.9995
Ozawa-Doyle	228.40		–	0.9995

Table 4. The lifetime of the complex [Sm(*o*–ClBA)$_3$phen]$_2$ by isothermal temperature TG

T / (K)	$\tau_{10\%}$ / (min)	T / (K)	$\tau_{10\%}$ / (min)
563.15	183.41	583.15	47.19
573.15	91.87	593.15	30.22

Experimental equipment and conditions

Elemental analysis was performed on a Carlo-Erba model 1106 elemental analyzer. The content of samarium was assayed using EDTA titration method. Infrared spectra were recorded over the range 4000-400 cm^{-1} using Bio-Rad FTS-135 spectrometer (KBr discs). X-ray diffraction data collection for a crystal with dimension 0.38 × 0.30 × 0.22 mm was performed on Bruker Apex IICCD diffractometer with graphite-monochromated Mo Kα radiation (λ=0.71073 Å) at 293K, using Φ-ω scan mode. A semi-empirical absorption correction based on SADABS was applied. 10701 Unique data (R_{int}=0.0172) were used to solve the structure by direct methods using SHELXS-97 program, and refined on F^2 by full-matrix least squares methods using SHELXL-97 program. All non-H atoms were refined anisotropically, and the H atoms were included in the structure-factor calculations. The crystal data and refinement details of the complex are summarized in Table 1. The TG and DTG experiments for the title compound were determined using a Perkin-Elmer's TGA7 Thermogravimetric analyzer under a nitrogen atmosphere, at a flow rate of 25 mL min^{-1}. The heating rate used was 3, 5 and 7 °C min^{-1} from ambient to 925 °C, respectively. The sample weight was 2.6±0.2mg.

Conclusions

The title complex [Sm(*o*–ClBA)$_3$phen]$_2$ were successfully synthesized in ethanol solution. Its crystal structure was determined by single crystal X-ray diffraction. The results show that the coordination number is nine and the coordination behavior of carboxylate groups with Sm^{3+} ion appears to three different coordination modes. Thermal decomposition mechanism of the complex was proposed. The values of E and ln$A$ for the first-step thermal decomposition were also determined. The Arrhenius equation can be expressed as $\ln k = 39.26–229.1\times10^3/ RT$. The lifetime equation at mass-loss of 10% was deduced as $\ln\tau = –26.8166+20319.94/T$.

Acknowledgments

This project was supported by the Natural Science Foundation of Hebei Province and Hebei Education Department and Hebei Normal University.

Supplementary Information

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 289363. Copies of the data can be obtained, free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).

References

1. Huang, C. H.; *Coordination Chemistry of Rare Earths*, Science press: Beijing, 1997, pp. 378-387 (in Chinese).
2. Li, X.; Zou, Y. Q.; *Z. Kristallogr. - New Cryst. Struct.* **2004**, *219*, 419.
3. Wang, R. F.; Wang, M. Z.; Jin, L. P.; Cai, G. L.; *J. Beijing Normal Univ.* (Nat. Sci. Ed.), (in Chinese). **1994**, *30*, 241.
4. Wang, R. F.; Wang, S. P.; Shi, S. K.; Zhang, J. J.; *Rare Met.* **2004**, *23*, 103.
5. Wang, R. F.; Wang, S. P.; Shi, S. K.; Zhang,J. J.; *J. Coord. Chem.* **2002**, *55*, 215.
6. Wang, R. F.; Wang, S. P.; Zhang, J. J.; *J. Mol. Struct.* **2003**, *648*, 151.
7. Wang, R. F.; Li, L. S.; Jin, L. P.; *J. Rare Earths* **1998**, *16*, 149.
8. Wang, R. F.; Jin, L. P.; Li, L. S.; Zu, L. S.; Zhang, J. H.; *J. Coord. Chem.* **1999**, *47*, 279.
9. Wang, R. F.; Wang, S. P.; Shi, S. K.; Zhang, J. J.; *Chin. J. Struct. Chem.* **2004**, *23,* 1300.
10. Zhang, J. J.; Wang, R. F.; Wang, S. P.; Liu, H. M.; Li, J. B.; Bai, J. H.; Ren, N.; *J. Therm. Anal. Calorim.*, **2005**, *79*,181.
11. Zhang, J. J.; Wang, R. F.; Liu, H. M.; Li, J. B.; Ren, N.; Gao, Z. H.; *Chin. J. Chem.* **2005**, *23,* 646.
12. Zhang, J. J.; Wang, R. F.; Li, J. B.; Liu, H. M.; *J. Therm. Anal. Calorim.* **2001**, *65*, 241.
13. Ren, N.; Zhang, J. J.; Xu, S. L.; Wang, R. F.; Wang, S. P.; *Thermochim. Acta* **2005**, *438*, 172.
14. Ren, N.; Zhang, J. J.; Wang, R. F.; Wang, S. P.; *J. Chin. Chem. Soc.* **2006**, *53*, 293.
15. Zhang, J. J.; Wang, R. F.; Wang, S. P.; Liu, H. M.; Li, J. B.; B, J. H.; *J. Therm. Anal. Calorim.* **2003**, *73*, 977.
16. Kissinger, H. E.; *Anal. Chem.* **1957**, *29*, 1702.
17. Ozawa, T.; *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1881.
18. Doyle, C. D. J.; *J. Appl. Polym. Sci.* **1961**, *5*, 285.
19. Wang, Z. L.; Jin, Z. S.; Niu, C. J.; Ni, J. Z.; *J. Rare Earths* **1992**, *10*, 102.
20. Bai, G. Z.; Chen, G. D.; Wang, Z. M. Yuan, L.; Kang, J. W.; Gao, J. Z.; *Chin. J. Inorg. Chem.* **1988**, *4*, 32.
21. Lam, A. W-H.; Wang, W. T.; Gao, S.; Wen, G. H.; Zhang, X. X.; *Eur. J. Inorg. Chem.* **2003**, 149.

Received: December 12, 2005
Published on the web: September 26, 2006