Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Synthesis, Crystal Structure, and Thermal Analysis of a 1D Coordination Compound $Cd(SCZ)Cl_2$ (SCZ=Semicarbazide)

Jian-Chao Liu, Wen-Chao Tong, Lin-Jun Xue, Tong-Lai Zhang & Li Yang

To cite this article: Jian-Chao Liu, Wen-Chao Tong, Lin-Jun Xue, Tong-Lai Zhang & Li Yang (2015) Synthesis, Crystal Structure, and Thermal Analysis of a 1D Coordination Compound $Cd(SCZ)Cl_2$ (SCZ=Semicarbazide), Molecular Crystals and Liquid Crystals, 616:1, 125-132, DOI: 10.1080/15421406.2014.927961

To link to this article: http://dx.doi.org/10.1080/15421406.2014.927961

Published online: 25 Sep 2015.

Mol. Cryst. Liq. Cryst., Vol. 616: pp. 125–132, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.927961

Synthesis, Crystal Structure, and Thermal Analysis of a 1D Coordination Compound $Cd(SCZ)Cl_2$ (SCZ=Semicarbazide)

JIAN-CHAO LIU, WEN-CHAO TONG, LIN-JUN XUE, TONG-LAI ZHANG, AND LI YANG*

State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing, P. R. China

A novel transition metal multiligand coordination compound $Cd(SCZ)Cl_2$ was synthesized and characterized by elemental analysis and FTIR spectroscopy. Single-crystal X-ray diffraction analysis revealed that $Cd(SCZ)Cl_2$ crystallizes in Orthorhombic *$Pna2_1$ space group. The thermal decomposition mechanism of $Cd(SCZ)Cl_2$ was studied by differential scanning calorimetry (DSC), which revealed that the complex contained one main endothermic process and one main exothermic process between 474 K and 648 K. The nonisothermal kinetics parameters were calculated by the Kissinger's method and Ozawa-Doyle's method, respectively.*

Keywords Cadmium(II); crystal structure; semicarbazide; thermal analysis

Introduction

Recently, nitrogen heterocyclic rings have obtained much attention as ligands to construct energetic coordination complexes, such as 3-azido-1,2,4-triazole [1–4], 5-nitrotetrazole [5–9], and 1,5-diaminotetrazole [10–14], due to the positive heat of formation and thermal stability. On the other side, oxygenic, and azotic chain ligands, such as carbohydrazide (CHZ) and semicarbazide (SCZ), have also attracted researcher's attention.

CHZ is a derivative of hydrazine. As an azotic and oxygenic ligand with lone electron pairs, its coordination modes can be various [15–20]. There are many reports on metal carbohydrazide complexes [21–26], which provide solid foundation for the application of the scientific achievements cadmium tri(carbohydrazide) perchlorate and zinc tri(carbohydrazide) perchlorate. SCZ is structurally similar to CHZ, whereas the literature for metal semicarbazide coordination compounds is rare. Zhang et al. investigated the crystal structure of $[Mn(SCZ)_3](PA)_2{\cdot}H_2O$ using X-ray single-crystal diffraction in 2004 [27], reporting that Mn^{2+} is hexacoordinated by the oxygen and nitrogen atoms of three SCZ molecules to form three stable five-membered rings. In 2007, Zhang et al. reported the crystal structure and thermal decomposition mechanisms of $Cu(SCZ)_2Cl_2$ and $[Ni(SCZ)_3](NO_3)_2$. In both compounds, semicarbazides coordinate to nickel(II) or copper(II) centers to form the five-membered ring system [28].

*Address correspondence to Dr. Li Yang, State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, P. R. China. E-mail: yanglibit@bit.edu.cn

In order to deepen the study on SCZ compound, herein we report a novel semicarbazide coordination compound $Cd(SCZ)Cl_2$, which was studied by its preparation, crystal structure, and thermal decomposition.

Experimental

Materials and Physical Techniques

All reagents (analytic grade) were purchased commercially and used without further purification. Elemental analyses were performed with a Flash EA 1112 full automatic trace element analyzer. The FT-IR spectra were recorded with a Bruker Equinox 55 infrared spectrometer (KBr pellets) in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. DSC measurement was performed with a Pyris-1 differential scanning calorimeter in a dry nitrogen atmosphere with flowing rate of 20 mL/min. The condition for the thermal analysis was as follow: the sample was powdered and sealed in the aluminum pans with a linear heating rate of 20 K/min from 400 K to 700 K.

Synthesis

Synthesis of $Cd(SCZ)Cl_2$ is similar to that of $Cu(SCZ)_2Cl_2$ and $[Ni(SCZ)_3](NO_3)_2$ [28]. Semicarbazide hydrochloride (1.11 g, 10 mmol) was dissolved in distilled water (10 ml) and the pH value was adjusted to 6–7 using 10% NaOH solution. The reaction solution was stirred with a mechanical agitator and heated to 338 K for using. And then a solution containing cadmium nitrate (1.18 g, 5 mmol) in distilled water (15 mL) was added to the above mixture during 20 min with continuous stirring and keeping at 333 K for another 20 min. Afterwards, the solution was cooled to the room temperature naturally. The precipitate was collected by filtration, washed with ethanol, and the product was dried in an explosion-proof dryer. Single crystals suitable for X-ray measurement were obtained by evaporation of the mother liquor at room temperature for 14 days. Elemental analysis calcd. for $Cd(SCZ)Cl_2$ (molar mass 258.38 g/mol) (%):C 4.64, H 1.94, N 16.26; Found (%): C 4.70, H 1.89, N 16.05. IR (cm^{-1}, KBr pellets): 3481(s), 3397(s), 3286(s), 3149(s), 1637(vs).

X-Ray Crystallography

The X-ray diffraction data collection was performed with a Rigaku AFC-10/Saturn 724^+CCD detector diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) with ϕ and ω modes at 153(2) K. The structure was solved by direct methods using SHELXS-97 [29] and refined by full-matrix least-squares methods on F^2 with SHELXL-97 [30]. All nonhydrogen atoms were obtained from the difference Fourier map and subjected to anisotropic refinement by full-matrix least squares on F^2. Detailed information concerning crystallographic data collection and structure refinement are summarized in Table 1.

Results and Discussion

Crystal Structure of $Cd(SCZ)Cl_2$

As shown in Table 1, $Cd(SCZ)Cl_2$ crystallizes with a orthorhombic unit cell in the space group $Pna2_1$, different from $Cu(SCZ)_2Cl_2$ and $[Ni(SCZ)_3](NO_3)_2$, which both belong to the monoclinic $P2_1/c$ space group, despite all the three compounds were obtained by the

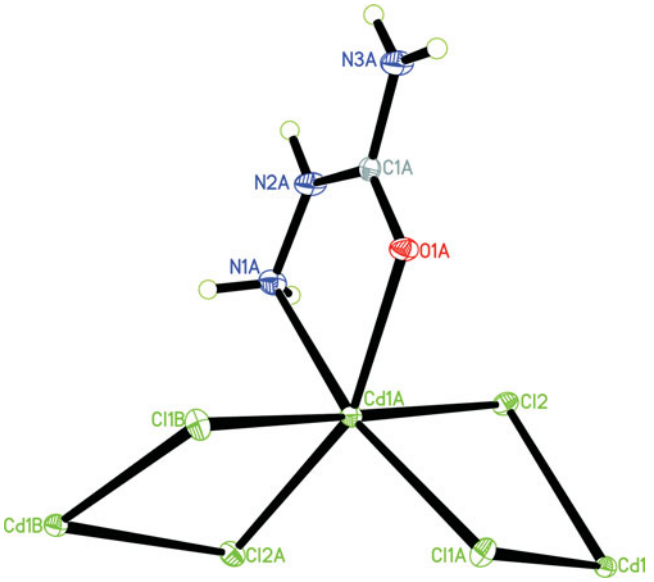

Figure 1. Molecular structure of $Cd(SCZ)Cl_2$.

Table 1. Crystallographic data and structure determination details

Empirical formula	$CH_5CdCl_2N_3O$
Formula weight	258.38
T/K	153(2)
Crystal system	*Orthorhombic*
Space group	$Pna2_1$
a/Å	6.8887(16)
b/Å	8.684(2)
c/Å	10.740(3)
V/Å^3	642.5(3)
Z	4
Crystal description	Chip
Crystal color	Colorless
D_c/(g•cm^{-3})	2.671
θ/(°)	3.02∼31.50
h, k, l	−10∼10, −10∼12, −15∼15
Reflections collections	2114
Independent reflection (R_{int})	2019(R_{int}=0.0301)
S	0.998
R_1, $wR_2[I > 2\sigma(I)]$[a]	$R_1 = 0.0233$,$wR_2 = 0.0393$
R_1, wR_2(all data)[a]	$R_1 = 0.0218$, $wR_2 = 0.0387$
μ(MoKα)/mm^{-1}	4.135
F(000)	488
CCDC	971239

[a] $w = 1/[\sigma^2(F_o^2) + (0.0236p)^2 + 0.1060p]$, $wR_2 = [\sum w(Fo^2–Fc^2)^2/\sum w(Fo^2)]^{1/2}$, $P = (Fo^2 + 2Fc^2)/3$.

Table 2. Selected bond lengths and angles for $Cd(SCZ)Cl_2$

Bond	Length/Å	Bond	Length/Å	Bond	Length/Å
Cd1A-O1A	2.276(2)	O1A-C1A	1.247(3)	N2A-C1A	1.355(4)
Cd1A-N1A	2.352(3)	N1A-N2A	1.402(4)	Cd1A-Cl1A	2.6618(8)
Cd1A-Cl1B	2.5273(8)	Cd1A-Cl2A	2.5813(8)	Cd1A-Cl2	2.7305(9)
Bond	Angle/°	Bond	Angle/°	Bond	Angle/°
O1A-Cd1A-N1A	71.98(8)	O1A-C1A-N3A	122.0(3)	C1A-O1A-Cd1A	116.31(18)
O1A-Cd1A-Cl1B	99.61(6)	O1A-C1A-N2A	122.1(3)	N2A-N1A-Cd1A	109.06(18)
N1A-Cd1A-Cl1A	168.12(7)	N3A-C1A-N2A	115.8(3)	C1A-N2A-N1A	119.5(3)
O1A-Cd1A-Cl2A	158.80(5)	N1A-Cd1A-Cl2A	91.25(7)	Cl1B-Cd1A-Cl2A	98.71(3)
Cl2A-Cd1A-Cl2	101.23(3)	Cl1B-Cd1A-Cl2	171.64(2)	Cd1A-Cl1A-Cd1	94.02(3)

similar reaction route [28]. The coordination environment of the cadmium cation and the molecular unit of $Cd(SCZ)Cl_2$, with atom labeling are demonstrated in figure 1. Selected bond lengths and angles for $Cd(SCZ)Cl_2$ are given in Table 2.

Molecular unit of $Cd(SCZ)Cl_2$ contain one cadmium cation, one neutral SCZ molecule, and two chloride ions. The central cadmium cation coordinates with six ligand atoms, four chlorides, one nitrogen atom, and one oxygen atom of SCZ. The chloride ions act as bridges connecting the central cations to each other. The bond lengths of the central cadmium(II) atom to coordinated atoms can be observed as Cd1A-O1A = 2.276(2) Å, Cd1A-N1A = 2.352(3) Å, Cd1A-Cl1B = 2.5273(8) Å, Cd1A-Cl1A = 2.6618(8) Å, Cd1A-Cl2A = 2.5813(8) Å, Cd1A-Cl2 = 2.7305(9) Å. The bond angels are 168.12(7)° (N1A-Cd1A-Cl1A), 158.80(5)° (O1A-Cd1A-Cl2A), and 171.64(2)° (Cl1B-Cd1A-Cl2), respectively, which obviously deviate from the ideal angle of 180°. These bond lengths and angles demonstrate that the cadmium(II) cation is coordinated to form a slightly distorted octahedral configuration.

There exist three planes in the molecular structure of $Cd(SCZ)Cl_2$. The equations and deviation of the planes are exhibited below:

Cd1A-N1A-N2A-C1A-O1A (plane A): $6.260x + 0.514y + 4.4362z = 8.2983$ with the deviation of 0.0406;

Cd1A-Cl1B-Cd1B-Cl2A (plane B): $-2.409x + 6.551y + 5.967z = 1.7976$ with the deviation of 0.1615;

Cd1A-Cl1A-Cd1-Cl2 (plane C): $2.409x + 6.551y - 5.967z = 0.2735$ with the deviation of 0.1616.

The angles between planes A and B, planes A and C, and planes B and C are 92.5°, 82.4°, and 82.1°. Plane B and C are almost vertical to each other, forming a 1D infinite chain along the *a* axis, as shown in figure 2. The chlorine plays a bridging role and the equivalent Cd(II) ions are bridged by two chloride atoms. Besides, there also exists a 1D channel in the crystal along the *b* axis (Figure 2).

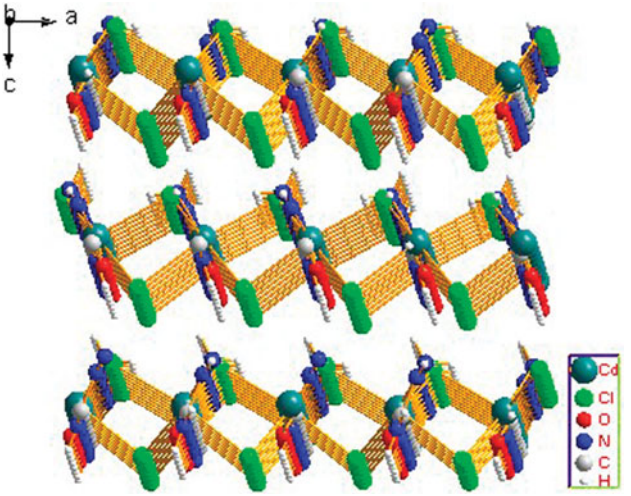

Figure 2. The 1D channel of Cd(SCZ)Cl$_2$.

Semicarbazide coordinates to cadmium(II) center to form a five-membered ring and there is one uncoordinated amino group connecting to the five-membered ring. The uncoordinated amino group is in a semi-dissociated state. This semi-dissociated structure leads to good molecule flexibility to the title complex. Besides, weak N—H···O hydrogen bonds among carbonyl and amino groups were observed in Cd(SCZ)Cl$_2$. It can be seen from the packing diagram (Figure 3) that all intermolecular and intramolecular hydrogen bonds extend the structure into a 3D supramolecular structure and make an important contribution to enhance the thermal stability of the complex.

Thermal Analysis

In order to investigate the thermal behavior of Cd(SCZ)Cl$_2$, DSC curve with a linear heating rate of 20 K/min was recorded (Figure 4). In the DSC curve, there is one endothermic peak

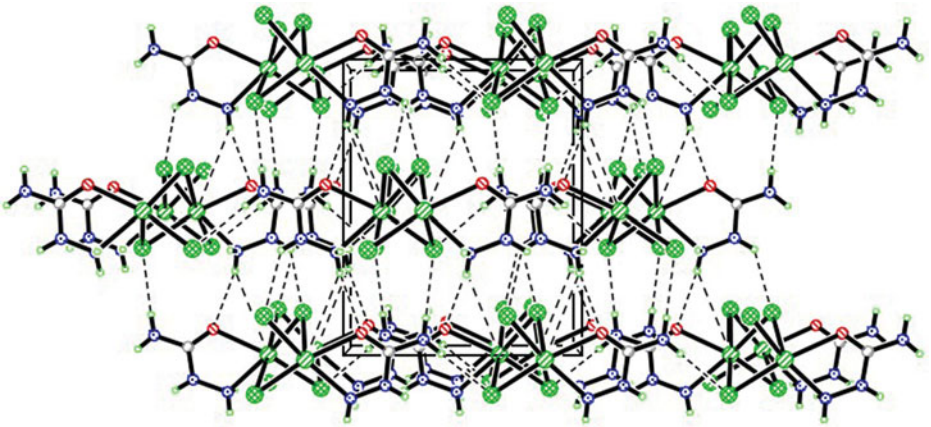

Figure 3. Packing plot of Cd(SCZ)Cl$_2$ viewed along the *a*-axis of the unit cell.

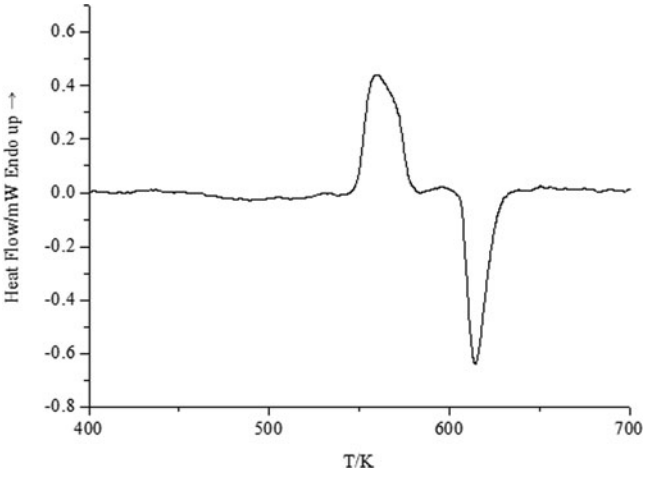

Figure 4. DSC curve of $Cd(SCZ)Cl_2$ under nitrogen with a heating rate of 20 K/min.

and one exothermic peak. The endothermic stage occurs in the range of 544.3 K∼582.5 K with a peak temperature of 559.8 K, while the exothermic process starts at 596.2 K and ends at 638.7 K with a peak temperature of 615.3 K. The DSC curve of $Cd(SCZ)Cl_2$ shows its potential as heat-resisting material with its endothermic peak temperature 560 K approximately and exothermic peak temperature above 610 K.

Nonisothermal Kinetics Analysis

In the present works, Kissinger's method [31] and Ozawa-Doyle's method [32,33] are widely used to determine the apparent activation energy (E) and the pre-exponential factor (A). The Kissinger and Ozawa-Doyle equations are as follows, respectively:

$$1n\beta/T_p^2 = 1n[RA/E] - E/(RT_p)$$

$$1g\beta = 1g[AE/RG(\alpha)] - 2.315 - 0.456E/RT_p$$

Where T_p is the peak temperature [K], A is the pre-exponential factor [s^{-1}], E is the apparent activation energy [kJ/mol], R is the gas constant (8.314 J/K/mol^{-1}), β is the linear heating rate [K/min], and G(α) is the reaction mechanism function.

Based on the first exothermic peak temperatures measured at four different heating rates of 5, 10, 15, and 20 K/min, Kissinger's method and Ozawa-Doyle's method were applied to study the kinetics parameters of $Cd(SCZ)Cl_2$. From the original data, the apparent activation energy E, pre-exponential factor A, linear coefficient R, and standard deviations S were determined and shown in Table 3.

So, the Arrhenius equation of $Cd(SCZ)Cl_2$ can be expressed as follows: (E is the average of E_k and E_o):

$$1nk = 74.91 - 393.9 \times 10^3/(RT)$$

The equation can be used to estimate the rate constants of the initial thermal decomposition process of the title compound.

Table 3. Peak temperatures of the first exotherm and the chemical kinetics parameters

β/(K/min)	T_p/K	Parameter	Kissinger's method	Ozawa's method
5	605.1	E/kJ/mol	398.8	388.9
10	608.0	lgA	32.53	—
15	611.4	R	−0.9649	−0.9665
20	615.3	S	0.1889	0.0820

Conclusions

A novel transition metal coordination polymer Cd(SCZ)Cl_2 was synthesized and characterized. In the compound, cadmium is six-coordinated with a distorted octahedral configuration by four chlorides, an oxygen atom and a nitrogen atom from one SCZ ligand, which forms a 1D channel and is connected to a 3D supramolecular structure through hydrogen bonds. Thermal analysis indicates that Cd(SCZ)Cl_2 has potential as heat-resisting material with its exothermic peak temperature above 610 K. Non-isothermal kinetics analysis reveals that the Arrhenius equation of Cd(SCZ)Cl_2 can be expressed as follows: $\ln k = 74.91–393.9 \times 10^3/(RT)$. As a continuous work on SCZs, the title complex has enriched the transition metal semicarbazide complex data base, providing solid foundation for the research of the metal semicarbazide complex.

Funding

The authors gratefully acknowledge the financial support from the State Key Laboratory of Explosion Science and Technology (No. QNKT12-02), and Science and Technology on Applied Physical Chemistry Laboratory (No. 9140C370303120C37142).

References

[1] Cui, Y., Zhang, T. L., Zhang, J. G., Yang, L., Zhang, J., & Hu, X. C. (2008). *Struct. Chem.*, *19*, 269.
[2] Cui, Y., Zhang, T. L., Zhang, J. G., & Yang, L. (2008). *Chinese J. Chem.*, *26*, 2021.
[3] Feng, J. L., Zhang, J. G., Zhang, T. L., & Cui, Y. (2010). *Acta Phys. Chim. Sin.*, *26*, 2410.
[4] Feng, J. L., Zhang, J. G., Li, Z. M., Zhang, T. L., Cui, Y., & Yang L. (2010). *Acta Chim. Sinica*, *68*, 2493.
[5] Talawar, M. B., Agrawal, A. P., Chhabra, J. S., Ghatak, C. K., Asthana, S. N., & Rao, K. U. B. (2004). *J. Sci. Ind. Res.*, *63*, 677.
[6] Talawar, M. B., Agrawal, A. P., & Asthana, S. N. (2005). *J. Hazard. Mater.*, *120*, 25.
[7] Huynh, M. H. V., Coburn, M. D., Meyer, T. J., & Wetzler, M. (2006). *Proc. Natl. Acad. Sci. USA.*, *103*, 10322.
[8] Klapötke, T. M., Sabaté, C. M., & Welch, J. M. (2008). *Dalton Trans.*, 6372.
[9] Klapötke, T. M., Sabaté, C. M., & Rasp, M. (2009). *Dalton Trans.*, 1825.
[10] Gaponik, P. N., Voitekhovich, S. V., Lyakhov, A. S., Mlatulis, V. E., Ivashkevich, O. A., Quesada, M., & Reedijk, J. (2005). *Inorg. Chim. Acta*, *358*, 2549.
[11] Cui, Y., Zhang, J. G., Zhang, T. L., Yang, L., Zhang, J., & Hu, X. C. (2008). *J. Hazard. Mater.*, *160*, 45.
[12] Cui, Y., Zhang, J. G., Zhang, T. L., Yang, L., Zhang, J., & Hu, X. C. (2008). *Propellants, Explos., Pyrotech.*, *33*, 437.

[13] Zhang, J. G., Li, Z. M., Zang, Y., Zhang, T. L., Shu, Y. J., Yang, L., & Power, P. P. (2010). *J. Hazard. Mater.*, *178*, 1094.
[14] Li, Z. M., Zhang, J. G., Cui, Y., Zhang, T. L., Shu, Y. J., Sinditskii, V. P., Serushkin, V. V., & Egorshin, V. Y. (2010). *J. Chem. Eng. Data*, *55*, 3109.
[15] Zhang, T. L., Lv, C. H., Qiao, X. J., & Cai, R. J. (1999). *Chinese J. Struct. Chem.*, *18*, 432.
[16] Lv, C. H., Zhang, T. L., Ren, L. B., Yu, K. B., Lu, Z., & Cai, R. J. (2000). *Chinese J. Explos. Propellants*, *8*, 31.
[17] Zhang, J. G., Zhang, T. L., Wei, Z. R., & Yu, K. B. (2001). *Chem. J. Chinese U.*, *22*, 895.
[18] Chen, H. Y., Zhang, T. L., Zhang, J. G., & Yu K. B. (2005). *Struct. Chem.*, *16*, 657.
[19] Sun, Y. H., Zhang, T. L., Zhang, J. G., Yang, L., & Qiao, X. J. (2006). *Acta Phys.-Chim. Sin.*, *22*, 649.
[20] Zhang, J. G., Zhang, T. L., & Yu, K. B. (2006). *Struct. Chem.*, *17*, 249.
[21] Sinditskii, V. P., Fogelzang, A. E., Dutov, M. D., Sokol, V. I., Serushkin, V. V., Svetlov, B. S., & Poraikoshits, M. A. (1987). *Zh. Neorg. Khim.*, *32*, 1944.
[22] Yang, Y. M., Zhang, T. L., Zhang, J. G., & Shao, B. (2002). *Chinese J. Struct. Chem.*, *21*, 321.
[23] Zheng, H., Zhang, T. L., Zhang, J. G., Qiao, X. J., Yang, L., & Sun Y. H. (2006). *Chinese J. Inorg. Chem.*, *22*, 346.
[24] Zhang, J., Zhang, T. L., Zhang, J. G., Yang, L., Cui, Y., Hu, X. C., & Liu, Z. H. (2008). *Struct. Chem.*, *19*, 321.
[25] Huang, H. S., Zhang, T. L., Zhang, J. G., & Wang, L. Q. (2010). *J. Hazard. Mater.*, *179*, 21.
[26] Li, Z. M., Zhang, J. G., Zhang, T. L., Yang, L., & Zhang, J. (2012). *J. Coord. Chem.*, *65*, 143.
[27] Ma, G. X., Zhang, T. L., Shao, B., Zhang, J. G., Song, J. C., Li, Y. F., & Yu, K. B. (2004). *Chin. J. Struct. Chem.*, *23*, 445.
[28] Guo, J. Y., Ma, G. X., Zhang, T. L., Zhang, J. G., & Liu, Y. H. (2007). *Trans. Meta. Chem.*, *32*, 413.
[29] Sheldrick, G. M. (1997). *SHELXS-97 Program for the Solution of Crystal Structure*, University of Göttingen: Germany.
[30] Sheldrick, G. M. (1997). *SHELXL-97, Program for Crystal Structure Refinement from Diffraction Data*, University of Göttingen: Germany.
[31] Kissinger, H. E. (1957). *Anal. Chem.*, *29*, 1702.
[32] Ozawa T. (1965). *Bull. Chem. Soc. Jpn.*, *38*, 1881.
[33] Doyle, C. D. (1961). *J. Appl. Polym. Sci.*, *5*, 285.