

4-Chloro-2-((E)-(Isopropylimino)methyl)phenol 코발트(II) 착물에 대한 결정 구조 및 열분해 연구

Xiao-Hua Pu*

Department of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences,
Baoji 721013, P. R. China

(접수 2010. 5. 24; 수정 2010. 11. 15; 게재확정 2011. 2. 21)

Crystal Structure and Thermal Decomposition Studies on Cobalt (II) Complex of 4-Chloro-2-((E)-(Isopropylimino)methyl)phenol

Xiao-Hua Pu*

Department of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences,
Baoji 721013, P. R. China. *E-mail: pxh913@163.com

(Received May 24, 2010; Revised November 15, 2010; Accepted February 21, 2011)

요약. Schiff base 코발트(II) 착물, bis[4-chloro-2-((E)-(isopropylimino) methyl) phenol]cobalt(II),을 합성하고 단결정 X-ray 회절 분석을 하였다. 코발트 (ii) 합성물의 현상학적, 속도론적 및 기계적 특성은 TG/DTG법으로 연구하였다. 실험 데이터에 기초하여, 활성화 에너지, 지수 앞자리인자, 활성화 엔트로피와 같은 속도론적 파라미터를 계산하였으며, 가장 가능성이 있는 메카니즘 함수로는 $g(\alpha)=\alpha^2$ 이 추정되었다. 따라서, 모든 분해 단계에서 속도 조절 단계는 1차원 확산 과정(Parabolic model) 이다.

주제어: 코발트(II) 착물, 결정 구조, Coats-Redfern, 분해, 속도론적, 가장 가능한 메카니즘

ABSTRACT. The Schiff base cobalt(II) complex, bis[4-chloro-2-((E)-(isopropylimino) methyl) phenol]cobalt(II), has been prepared and characterized by single-crystal X-ray diffraction analyses. The phenomenological, kinetic and mechanistic aspects of the cobalt (II) complex have been studied by TG/DTG techniques. On the basis of the experimental data, the kinetic parameters such as activation energy, pre-exponential factor and entropy of activation were computed, and then the most probable mechanism function was estimated as $g(\alpha)=\alpha^2$. Hence the rate controlling process at all stages of decomposition is one-dimensional diffusion (Parabolic model).

Keywords: cobalt(II) complex, crystal structure, Coats-Redfern, decomposition, kinetic, most probable mechanism

INTRODUCTION

Transition metal complexes containing oxygen and nitrogen donor Schiff base ligands had been of research interest for many years for their industrial and biological applications.¹⁻⁴ Li *et. al.* had reported the crystal structure of bis[4-chloro-2-(cyclohexylim-inomethyl)-phenolato]-cobalt(II) and bis[4-chloro-2-(cyclohexyliminomethyl)-phenolato]zinc(II),⁵⁻⁶ which are of great interests in coordination chemistry in relation to catalysis and enzymatic reactions, magnetism and molecular architectures. The symmetrical bis(aza crown ether)s cobalt(II) complexes had been prepared and had proven to be a model to mimic hydrolase in PNPP hydrolysis.⁷ A wide variety of cobalt(II) complexes had been studied as model compounds for natural oxygen carriers and for their use in O₂ storage.⁸ Even

though many Schiff bases using 5-Chlorosalicylaldehyde and amines had been studied,⁹⁻¹² as ligands, no work had been done with 5-chlorosalicylaldehyde and isopropylamine as the basic nucleus of Schiff bases. In addition, the thermal behaviour of this type of complex is almost unknown, because systematic thermal analysis has not been carried out.

In this paper, we report synthesis and thermal behaviour of a new cobalt(II) complex, bis[4-chloro-2-((E)-(isopropylimino)methyl)phenol]cobalt(II) (Scheme 1). The structure of the complex had been established accurately from the single crystal X-ray diffraction study. The Co(II) ion in the monomeric unit seems to reside in a distorted tetrahedral environment and bonds to two oxygen atoms and two nitrogen atoms from two Schiff bases. Thermal studies supported the chemical formulation of the complex

and showed that the complex decomposes in four steps. The kinetic parameters such as activation energy, pre-exponential factor and entropy of activation of the complex were calculated. The mechanism for the thermal decomposition process was also proposed.

EXPERIMENTAL

Physical measurements

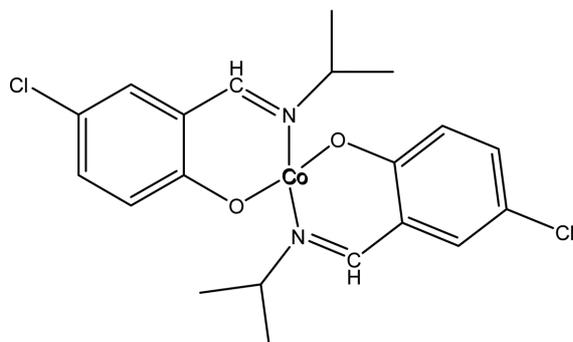
Thermogravimetric analyses were carried out on a Pyris Diamond TG/DTA SII thermal analyzer, Perkin Elmer. Instrument calibration was performed with standard indium samples of known melting temperature. For the kinetics measurements, about 3 mg sample was weighted in to an open platinum crucible. The selected heating rate was 5 K.min⁻¹, and nitrogen gas of high purity (> 99.999%) with a flow rate of 50 mL min⁻¹ was used as carrier gas. The kinetic evaluation of the thermal decomposition of the complex was done using origin 8.0.

Synthesis of the complex

To the vigorously stirred solution of 5-Chlorosalicylaldehyde (0.1 mmol, 15.7 mg) in EtOH (1 cm³), was added dropwise a colourless solution of isopropylamine (0.1 mmol, 5.9 mg) in solution of EtOH (1 cm³) with stirring at room temperature for 1 h. To the resulting orange solution was added Co(NO₃)₂·6H₂O 0.1 mmol, 35.3 mg). The mixture was stirred for 1 h. Dark red block-shaped crystals of the title complex grew after two weeks. The product was filtered, washed with EtOH, and dried over anhydrous CaCl₂ in vacuo overnight. Yield: 90%. Anal. Calcd. (%) for (C₂₀H₂₂CoN₂O₂Cl₂): C, 54.09; H, 5.19; N, 6.01. Found (%): C, 54.13; H, 5.21; N, 6.05.

X-ray single crystal structure determination

A dark red block crystal of the title complex having approximate dimensions of 0.26 mm × 0.22 mm × 0.11 mm



Scheme 1. The structure of the title complex.

was mounted on a glass fiber in a random orientation. The data were collected on a Bruker SMART 1000 CCD diffractometer at 298(2) K. The unit cell parameters and data collections were performed using Bruker SMART program¹³ with graphite-monochromatic *MoKα* radiation ($\lambda=0.71073\text{Å}$). Semiempirical absorption correction was applied by using the SADABS program.¹⁴ The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using the SHELXL-97 program package.¹⁵ All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at their idealized positions. The crystal data and structure refinement parameters for the complex are summarized in *Table 1*. Selected bond lengths and angles are given in *Table 2*.

Table 1. Crystal data and structure refinement parameters

Properties	Complex
Empirical formula	C ₂₀ H ₂₂ CoN ₂ O ₂ Cl ₂
Formula weight	452.23
Temperature/K	298(2)
Radiation(<i>MoKα</i>), $\lambda(\text{Å})$	0.71073
Crystal shape/color	block/red
Crystal size (mm ³)	0.26 × 0.22 × 0.11 mm
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> (Å)	10.2001(10)
<i>b</i> (Å)	9.6380(9)
<i>c</i> (Å)	22.020(2)
β (°)	102.440(2)
<i>V</i> (Å ³)	2113.9(4)
<i>Z</i>	4
<i>D_c</i> (g/cm ³)	1.421
μ (mm ⁻¹)	1.081
<i>F</i> (0 0 0)	932
θ range (°)	1.89/25.02
Index range (<i>h, k, l</i>)	-12/6, -11/11, -26/25
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8903 and 0.7663
Measured reflections	1861
Observed reflections [$I \geq 2\sigma(I)$]	1266
Data/restraints/parameters	1861/0/125
Goodness-of-fit on F^2	1.056
<i>R</i> ₁ , <i>wR</i> ₂ [$I \geq 2\sigma(I)$]	0.0476/0.1165
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0734/0.1273
Large diff. peak and hole (e.Å ⁻³)	0.383 and -0.232
$(\Delta/\sigma)_{\text{max}}$	0.060

Note: $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \sum [w(F_o^2 - F_c^2)]^{1/2} / \sum w(F_o^2)^{1/2}$, $w_1 = [\sigma^2(F_o^2) + (0.0612(F_o^2 + 2F_c^2)/3)^2 + 0.0000(F_o^2 + 2)/3]^{-1}$

Table 2. Selected bond lengths and bond angles

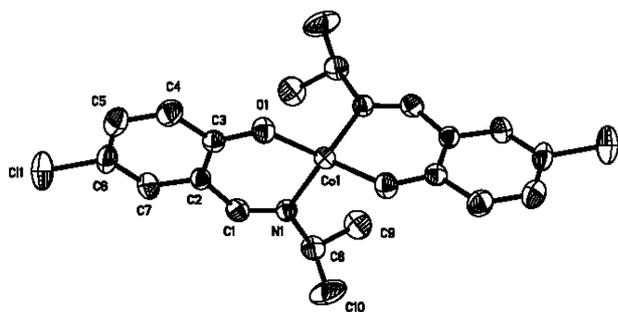
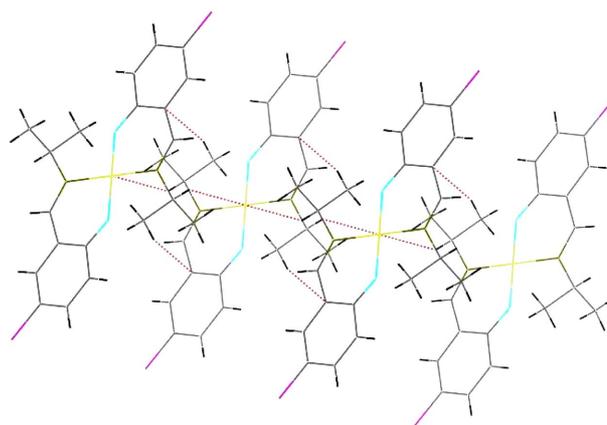
Bond lengths	(Å)	Bond angles	(°)
Co(1)-O(1)	1.913(3)	O(1)-Co(1)-O1A	119.79(15)
Co(1)-O1A	1.913(3)	O(1)-Co(1)-N1A	114.03(12)
Co(1)-N1A	1.992(3)	O1A-Co(1)-N1A	96.39(11)
Co(1)-N(1)	1.992(3)	O(1)-Co(1)-N(1)	96.39(11)
Cl(1)-C(6)	1.744(4)	O1A-Co(1)-N(1)	114.03(12)
O(1)-C(3)	1.310(4)	N1A-Co(1)-N(1)	117.75(17)
N(1)-C(1)	1.280(5)	C(3)-O(1)-Co(1)	124.5(2)
		C(1)-N(1)-C(8)	118.0(3)
		C(1)-N(1)-Co(1)	120.1(3)
		C(8)-N(1)-Co(1)	122.0(2)

Symmetry codes: (A) $-x+1, y, -z+3/2$

RESULTS AND DISCUSSIONS

Description of the crystal structure

The structure of the complex including atom-numbering scheme, is shown in *Fig. 1*. The X-ray diffraction analysis of the complex shows, that the central cobalt(II) atom is four coordinate and bonds to two nitrogen atoms and two oxygen atoms from two 4-chloro-2-((E)-(isopropylimino)methyl)phenol Schiff bases in the usual *trans* arrangement. Each Schiff base acts as a bidentate ligand. The geometry around cobalt(II) is in a distorted tetrahedral environment, where the dihedral angle between the two coordination planes defined by O1Co1N1 and O1ACo1N1A is 86.60°, nearly perpendicular, which could be interpreted in terms of the isopropyl substituent having a bigger steric effect than the diphenylmethyl substituent on the geometry of these kinds of complexes.¹⁶ The phenyl ring plane (C2/C3/C4/C5/C6/C7) and the chelate ring (O1/Co1/N1/C1/C2/C3) are nearly coplanar with a dihedral angle of 3.4(2)°. This is true of the corresponding planes which were generated by symmetry. Bond angles also show that the coordination geometry about the cobalt atom is a distorted tetrahedral structure, with O1Co1N1, N1Co1N1A and O1Co1O1A angles of 96.39(11),

**Fig. 1.** Molecular structure of the title complex. Displacement ellipsoids are drawn at the 30% probability level.**Fig. 2.** The packing structure of the complex along the *b*-axis, showing the formation of 1D-chains by weak intermolecular Co...H interactions and weak hydrogen bonds C9-H9...C2.

117.75(17) and 119.79(15), respectively. The Co1O1 and Co1N1 distances are 1.913(3) and 1.992(3) Å, respectively, which are approached to the values found in other four coordinate cobalt complexes with similar ligands.^{5,8} Discrete monomeric molecules in both structures are held together by weak intermolecular interactions of cobalt atom with H8 and weak hydrogen bonds C9-H9...C2, which connect the independent molecules to form a one-dimensional chain (*Fig. 2*).

Phenomenological aspect

The thermal behavior of the complex was characterized using TG/DTG methods. The TG/DTG measurements of the complex were carried out within a temperature range from room temperature up to 800 °C. Typical thermogram of the complex is shown in *Fig. 3*. The complex undergoes a four-stage decomposition pattern in the range 107-582 °C. The first decomposition stage starts at 107 and ends at 167 °C with the DTG peak at 133 °C. The corresponding mass loss (9.5%) is attributed to the loss of the adsorbed water molecules.¹⁷ The second stage of decomposition starts at 194 and comes to an end at 345 °C with the DTG peak at 330 °C. The corresponding mass loss is 11.57% (calcd. 12.17%), which is associated with the decomposition of one (CH₃)₂C-N group of the ligand. Partial decomposition starts with the third step, which follows immediately after the second step in the 345-414 °C range with DTG peak at 387 °C. This step includes separation of the other (CH₃)₂C-N from the ligand with a mass loss 11.21% (calcd. 12.17%). The remaining part of the ligand is lost in the 414-590 °C range where the final decomposition takes place at 520 with metal carbonate as the residue.¹⁸

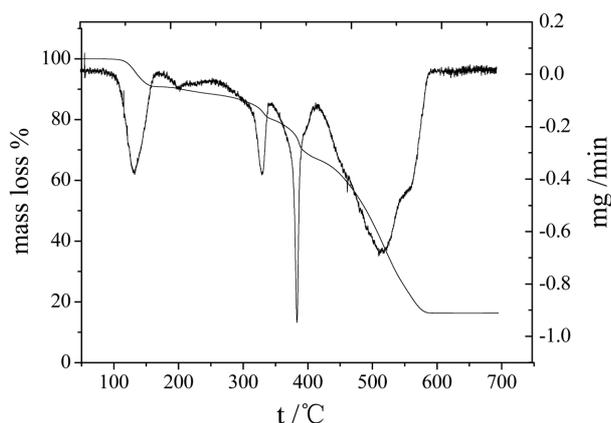


Fig. 3. TG and DTG curves of the complex.

Kinetic aspect

According to non-isothermal kinetic theory, thermal decomposition process can be described by Coats-Redfern equation.¹⁹

$$\log\left[\frac{g(\alpha)}{T^2}\right] = \log\frac{AR}{\phi E_a}\left[1 - \frac{2RT}{E_a}\right] - \frac{E_a}{2.303RT}$$

The kinetic parameters such as the activation energy (E_a) and the pre-exponential factor (A) are also calculated by this equation, where T —absolute temperature, A —pre-exponential factor, R —gas constant, ϕ —heating rate and E_a —activation energy.

The assignment of the specific mechanism of thermal decomposition is based on the assumption that the form of $g(\alpha)$ depends on the reaction mechanism. On plotting $\log[g(\alpha)/T^2]$ vs. $10^3/T$ calculated from TG trace for thirty-seven types²⁰ of mechanism functions, the most probable mechanism corresponding to the linear plot can be estimated.²¹

The correlation coefficient r (as shown in Table 3) are obtained by plotting $\log[g(\alpha)/T^2]$ vs. $10^3/T$. The parameters show that the correlation coefficient of No. 1 is better than others, and therefore $g(\alpha)=\alpha^2$ would be the most probable mechanism function in all stages of decomposition. The mechanism of decomposition is one-dimensional diffusion. This represents the “Parabolic model”.

The entropy of activation (ΔS) is also calculated for each stage of thermal decomposition in the complex using the following relationship,

$$A = \frac{kT_s}{h} e^{\frac{\Delta S}{R}}$$

where A —pre-exponential factor, k —Boltzmann constant, T_s —peak temperature, ΔS —entropy of activation and R —

Table 3. Correlation coefficients calculated using thirty-seven forms of $g(\alpha)$ for the complex

NO.	$g(\alpha)$	Correlation coefficient (r)		
		Stage II	Stage III	Stage IV
1	α^2	0.99638	0.99299	0.99408
2	$\alpha+(1-\alpha)\ln(1-\alpha)$	0.99635	0.99301	0.98836
3	$[1-(1-\alpha)^{1/3}]^2$	0.9963	0.99299	0.97873
4	$\left(1-\frac{2\alpha}{3}\right)-(1-\alpha)^{2/3}$	0.99633	0.99301	0.98499
5	$[(1+\alpha)^{1/3}-1]^2$	0.99636	0.99274	0.9947
6	$\left[(1-\alpha)^{\frac{1}{3}}-1\right]^2$	0.9962	0.99292	0.96153
7	$-\ln(1-\alpha)$	0.99502	0.98824	0.96351
8	$[-\ln(1-\alpha)]^{\frac{2}{3}}$	0.99303	0.9762	0.95461
9	$[-\ln(1-\alpha)]^{\frac{1}{2}}$	0.98954	0.92792	0.94192
10	$[-\ln(1-\alpha)]^{\frac{1}{3}}$	0.96492	0.82967	0.89315
11	$[-\ln(1-\alpha)]^{\frac{1}{4}}$	0.32349	0.98546	0.74954
12	$1-(1-\alpha)^{\frac{1}{4}}$	0.99498	0.98768	0.97008
13	$1-(1-\alpha)^{\frac{1}{3}}$	0.99496	0.98747	0.97232
14	$1-(1-\alpha)^{\frac{1}{2}}$	0.99493	0.98699	0.97681
15	α	0.99478	0.98493	0.98997
16	$\alpha^{\frac{3}{2}}$	0.99594	0.99125	0.99307
17	$\alpha^{\frac{1}{2}}$	0.98518	0.01715	0.91321
18	$\alpha^{\frac{1}{3}}$	0.85208	0.98554	0.95215
19	$\alpha^{\frac{1}{4}}$	0.92249	0.9966	0.99448
20	$-\ln(1-\alpha)$	0.99502	0.98824	0.96351
21	$(1-\alpha)^{-\frac{1}{2}}-1$	0.99506	0.98905	0.95159
22	$(1-\alpha)^{-1}-1$	0.99508	0.98961	0.94217
23	$[1/(1-\alpha)]^2$	0.98954	0.98171	0.92104
24	$1-(1-\alpha)^2$	0.99417	0.97347	0.18134
25	$1-(1-\alpha)^3$	0.99272	0.82434	0.98865
26	$1-(1-\alpha)^4$	0.9888	0.96918	0.99746
27	$[-\ln(1-\alpha)]^2$	0.99625	0.99296	0.96999
28	$[-\ln(1-\alpha)]^3$	0.99656	0.99391	0.97176
29	$[-\ln(1-\alpha)]^4$	0.9967	0.99431	0.97259
30	$\left[1-(1-\alpha)^{\frac{1}{2}}\right]^{\frac{1}{2}}$	0.98787	0.81338	0.94615
31	$\left[1-(1-\alpha)^{\frac{1}{3}}\right]^{\frac{1}{2}}$	0.98851	0.87381	0.94555
32	$\left[1-(1-\alpha)^{\frac{1}{2}}\right]^2$	0.99632	0.993	0.98299
33	$[-\ln(1-\alpha)]^{0.4}$	0.9825	0.33996	0.923
34	$[-\ln(1-\alpha)]^{1.5}$	0.9959	0.99177	0.96804
35	$[-\ln(1-\alpha)]^{0.75}$	0.99381	0.98173	0.95791
36	$3\left[1-(1-\alpha)^{\frac{1}{3}}\right]$	0.99496	0.98747	0.97232
37	$2\left[1-(1-\alpha)^{\frac{1}{2}}\right]$	0.99493	0.98699	0.97681

Table 4. Kinetic parameters for thermal decomposition of the complex

Stage	$E_a/\text{kJ}\cdot\text{mol}^{-1}$	A/s^{-1}	$\Delta S/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
II	58.40644	594.97	-192.66
III	32.33933	330.40	-198.87
IV	48.18225	490.13	-198.05

gas constant.

The activation energy (E_a), pre-exponential factor (A) and entropy of activation (ΔS) for stages II-IV of decomposition are listed in Table 4. The negative values of entropy of activation indicate that the activated complex has a more ordered structure than the reactants.²²

CONCLUSIONS

A new complex of Co(II) with Schiff base was synthesized and the structure was determined by X-ray crystallography study.

The TG data reveal that the complex undergoes a four-stage solid state thermal decomposition pattern. The kinetic model function was $g(\alpha)=\alpha^2$. The kinetic parameters such as activation energy, pre-exponential factor and entropy of activation of the complex were calculated. The mechanism for the different decomposition stages is found to be one-dimensional diffusion (Parabolic model).

Supplementary material: CCDC 773456 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax:+44(0)1223-336033; email: deposit@ccdc.cam.ac.uk].

Acknowledgement. We are grateful to the support of the research grant of Phytochemistry Key Laboratory of Shaanxi Province of the People's Republic of China. (No. 09JS068).

REFERENCES

- Chen, D.; Martell, A. E.; Sun, Y. Z. *Inorganic Chemistry* **1989**, *13*, 2647.
- Elmali, A.; Zeyrek, C. T.; Elerman, Y.; Durlu, T. N. *Journal of Chemical Crystallography* **2000**, *3*, 167.
- Chakraborty, J.; Samanta, B.; Pilet, G.; Mitra, S. *Struct. Chem.* **2006**, *17*, 585.
- Yilmaz, I.; Ilhan, S.; Temel, H.; Kilic, A. *J. Incl. Phenom. Macrocycl. Chem.* **2009**, *63*, 163.
- Li, Z. X.; Zhang, X. L. *Acta. Cryst.* **2005**, *E61*, o2806.
- Li, Z. X.; Zhang, X. L. *Acta. Cryst.* **2005**, *E61*, m1755.
- Zhang, C. G.; Tian G. H.; Liu, B. *Transition Metal Chemistry* **2000**, *25*, 377.
- Deligönlü, N.; Tümer, M.; Serin, S. *Transition Metal Chemistry* **2006**, *31*, 920.
- Li, Z. X.; Zhang, X. L.; Wang, X. L. *Acta. Cryst.* **2006**, *E62*, o4513.
- Zhang, X. L.; Li, Z. X. *Acta. Cryst.* **2007**, *E63*, o319.
- Kabak, M.; Elmali, A.; Kavlakoglu, E.; Elerman, Y.; Durlu, T. N. *Acta. Crystallogr.* **1999**, *C55*, 1650.
- Patel, N. H.; Parekh, H. M.; Patel, M. N. *Transition Metal Chemistry* **2005**, *30*, 13.
- Bruker (2000). SMART (Version 5.0) and SAINT (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. SHELXTL. *Structure Determination Software Suite*. Siemens Industrial Automation, Analytical Instrumentation, USA, 1995.
- Sheldrick, G. M. SADABS. *Siemens area detector absorption (and other) correction*. University of Göttingen: Germany, 1997.
- Fernández-G, J. M.; Ruiz-Ramírez, O. L.; Toscano, R. A.; Macías-Ruvalcaba, N.; Aguilar-Martínez, M. *Transition Metal Chemistry* **2000**, *25*, 511.
- Deligönlü, N.; Tümer, M. *Transition Metal Chemistry* **2006**, *31*, 920.
- Mohamed, G. G.; Abd El-Wahab, Z. H. *Journal of Thermal Analysis and Calorimetry* **2003**, *73*, 347.
- Coats, A.W.; Redfern, J. P. *Nature* **1964**, *201*, 68.
- Hu, R. Z.; Gao, S. L.; Zhao, F. Q.; Shi, Q. Z.; Zhang, T. L.; Zhang, J. J. *Thermal analysis kinetics* (section two) Science press: Perkin, China, 2008.
- Satava, V. *Thermochim. Acta.* **1971**, *2*, 423.
- Mathew, S.; Nair, C. G. R.; Ninan, K. N. *Thermochim. Acta.* **1989**, *155*, 247.