Synthesis, Crystal Structure, and Thermochemical Properties of a Copper(II) Complex $[Cu(BTZ)(DMF)Cl]_2$ [BTZ = 2-(2-Hydroxyphenyl)benzothiazolate]

Fei Liu, Lijun Wang, Fushan Yu, Lingling Zhang, Qi Wu, Yaoni Shi, and Xuwu Yang*

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, College of Chemistry and Materials Science, Northwest University, Xi'an, 710069, PR China

---

A new complex, $[Cu(BTZ)(DMF)Cl]_2$ [BTZ = 2-(2-hydroxyphenyl)benzothiazolate, DMF = *N*,*N*-dimethylformamide], was synthesized and characterized by X-ray crystallography, elemental analysis, IR spectrum, and TG−DTG. The results show that the complex crystallizes in a monoclinic space group *P*21/*c*; $a = 10.478(3)$ Å, $b = 8.993(3)$ Å, $c = 18.482(6)$ Å; $\beta = 105.697(5)°$; $V = 1676.59$ Å^3; and $Z = 4$. The structure of the complex is dimeric $[Cu(BTZ)(DMF)Cl]_2$ with two isotropic Cu^{2+} ion centers having five-coordinate geometry. The constant-volume combustion energy of the complex, $\Delta_c U$, was determined as being $(-17\,689.56 \pm 6.77)$ kJ·mol^{-1} by a precise rotating-bomb calorimeter (RBC-type II). The standard molar enthalpy of combustion, $\Delta_c H_m^\theta$, and the standard molar enthalpy of formation, $\Delta_f H_m^\theta$, were calculated at 298.15 K as being $(-17\,706.91 \pm 6.77)$ kJ·mol^{-1} and (-738.67 ± 7.96) kJ·mol^{-1}, respectively.

Introduction

Thermochemistry, to the best of our knowledge, is the basis of modern material science. The determination of heat effects which materials produce during physical and chemical changes may play a vital role in the materials application. Therein, the standard molar enthalpy of formation of a substance is of basic use in calculating the enthalpy change for a chemical reaction[1] and the corresponding lattice enthalpy obtained from the enthalpy of formation in the crystalline state.[2] The combustion calorimetry technique is the most widely used for determining the standard molar enthalpy of formation.[3–8] Exact thermodynamic data are urgently required as a basis of theoretical calculation of quantum chemistry, computer-aided molecular design of drugs and new materials, technological processes of synthesis and purification, and biochemical reactions. Hence, the performed quantitative studies on the energy data may be of great help to make further study of complexes that span from theoretical research to practical application.

Over the past decades, extensive research has been carried out in the aspect of transition metal complexes involving benzothiazolate derivatives due to their significantly different biological activity, catalytic activity and luminescent and magnetic properties.[9–12] As one of the benzothiazolate derivatives, 2-(2-hydroxyphenyl)benzothiazolate (BTZ) is a novel N,O-donor chelating ligand that can form multifunctional complexes with metal ions. Several metal complexes with BTZ have recently received relatively more attention on their applications as organic light-emitting diodes because of excellent electroluminescent properties.[13–17] Considering the biological activity of benzothiazolate derivatives, copper as an essential microelement for the human body, and the sparse research on their thermochemical properties, it is therefore of importance to investigate the BTZ complex with copper as the center ion. Our research group recently prepared transition metal complexes associated with the BTZ ligand and studied their thermochemical properties. In this paper, the BTZ complex of copper(II) was successfully synthesized; the crystal structure was studied; and its constant-volume combustion energy, $\Delta_c U$, was determined by a precise rotating-bomb calorimeter (RBC-type II). According to the value of $\Delta_c U$, the standard molar enthalpy of combustion, $\Delta_c H_m^\theta$, and the standard molar enthalpy of formation, $\Delta_f H_m^\theta$, were derived at 298.15 K.

Experimental Section

Materials and Instruments. All the reagents were of analytical grade and used without further purification except for benzoic acid and the BTZ ligand. Benzoic acid was purchased from the Shanghai Reagent Company, with mass fraction purity 0.99999, and dried in a vacuum oven prior to use. BTZ was synthesized according to the literature method.[18]

The C, H, and N contents were measured by a Vario EL III elemental analyzer (Germany). The standard deviation for C, H, and N is < ± 0.1 %. IR spectra (KBr pellet) were recorded with a model EQUINOX55 FT-IR spectrophotometer (Bruker, Germany; the resolution was ± 4 cm^{-1}). The thermal analysis TG-DTG experiment of the complex was performed using a Perkin-Elmer thermogravimetric instrument under a nitrogen atmosphere at a flow rate of 60 cm^3·min^{-1}. The heating rate used was 10 K·min^{-1} from ambient temperature to 1273 K, with a sample weight of about 5 mg. The constant-volume combustion energy of the complex was determined with RBC-type II.

Synthesis of the Complex. A mixture of $CuCl_2 \cdot 2H_2O$ (1 mmol, in 20 mL of acetone) and 2-(2-hydroxyphenyl)benzothiazolate (1 mmol, in 20 mL of DMF) was stirred at room temperature for 1 h. Then it was filtered, and the filtrate was allowed to evaporate very slowly. After three weeks, some dark red, rhombus single crystals of the complex were obtained in the mother liquid. The product was isolated, washed with deionized water and DMF, and dried in a vacuum desiccator over P_4O_{10}. The yield was 56 % based on BTZ. Anal. Calcd for $C_{16}H_{15}ClCuN_2O_2S$ (%): C, 48.24; H, 3.80; N, 7.03. Found: C, 48.30; H, 3.71; N, 7.10.

---

* Corresponding author. Tel.: +86-29-88302054. Fax: +86-29-88303798. E-mail: yangxuwu@nwu.edu.cn.

10.1021/je900651u

Table 1. Crystallographic Data and Structure Refinement Parameters for the Title Complex

empirical formula	$[C_{16}H_{15}ClCuN_2O_2S]_2$
formula weight	796.744
temperature (K)	296 (2)
wavelength (Å)	0.71073
crystal system	monoclinic
space group	*P*21/*c*
unit cell dimensions	$a = 10.479(3)$ Å, $\alpha = 90°$ $b = 8.993(3)$ Å, $\beta = 105.697(5)°$ $c = 18.482(6)$ Å, $\gamma = 90°$
volume (Å^3)	1676.7(9)
Z	4
calculated density (mg·m^{-3})	1.578
absorption coefficient (mm^{-1})	1.595
F (000)	812
crystal size (mm)	0.24 × 0.21 × 0.16
range for data collection (deg)	2.30 to 21.69
limiting indices	$-12 \le h \le 7$, $-10 \le k \le 10$, $-21 \le l \le 22$
reflections collected/unique	8125/2986 [R(int) = 0.0757]
completeness to $\theta = 25.10$ (%)	99.7
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	2986/0/210
goodness-of-fit on F^2	1.014
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0419$, $wR2 = 0.0916$
R indices (all data)	$R1 = 0.0744$, $wR2 = 0.1198$
largest diff. peak and hole (e·Å^{-3})	0.393 and −0.597

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Title Complex[a]

Cu(1)−O(1)	2.032(3)	N(1)−Cu(1)−O(2)	86.87(15)
Cu(1)−O(2)	2.177(3)	O(1)#1−Cu(1)−O(2)	88.27(13)
Cu(1)−O(1)#1	1.972(3)	O(1)−Cu(1)−O(2)	101.39(12)
Cu(1)−N(1)	1.968(4)	N(1)−Cu(1)−Cl(1)	98.84(11)
Cu(1)−Cl(1)	2.2495(14)	O(1)#1−Cu(1)−Cl(1)	94.97(9)
O(1)#1−Cu(1)−O(1)	77.78(14)	Cu(1)#1−O(1)−Cu(1)	102.22(14)
N(1)−Cu(1)−O(1)	89.76(14)	O(1)−Cu(1)−Cl(1)	130.36(9)
N(1)−Cu(1)−O(1)#1	165.46(13)	O(2)−Cu(1)−Cl(1)	127.70(10)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y + 2, -z$.

X-ray Data Collection and Structure Determination. The X-ray single crystal data collection for the complex was performed on a Bruker Smart Appex II CCD diffractometer, using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at 296(2) K. Absorption corrections were applied by SADABS. The structure was solved by a direct method with the SHELXL-97[19] program and refined with full-matrix least-squares methods. The non-hydrogen atoms were located with difference Fourier synthesis, and the hydrogen atoms were generated geometrically. Crystallographic data and structure refinement parameters for the title complex are summarized in Table 1, and selected bond lengths and angles are listed in Table 2.

Rotating-Bomb Combustion Calorimetry. The constant-volume combustion energy of the complex was determined with RBC-type II. The main experimental procedures were described previously.[20] This instrument was developed in our laboratory, and the calorimeter mainly consists of a water thermostat, a calorituber, and the system for temperature measurement. The bicyclical structure is used as the holder for the crucible support in the oxygen bomb, which facilitates the crucible stable relative to the bomb when the bomb was rotated in crosswise direction and vertically, assuring that the stable final state is attained in a short time.

The initial temperature of the combustion reaction was maintained at $T = (298.1500 \pm 0.0005)$ K, and the initial oxygen pressure was 2.5 MPa. In this investigation, 40 cm^3 of aqueous solution of As_2O_3 (0.09264 mol·dm^{-3}) as an initial bomb solution was added into the bomb. The added arsenious oxide solution ensured that all the free chlorine formed in the combustion experiment was reduced to aqueous hydrochloric acid.

The analytical methods of final products (gas, liquid, and solid) from the title complex combustion experiment were as reported in refs 5 and 20. The gaseous sulfurous anhydride produced during the process of the combustion reaction was converted catalytically to sulfur trioxide, where the platinum lining of the interior surfaces of the bomb acted as a catalyst. The bomb solution then absorbed the gaseous sulfur trioxide, generating aqueous sulfuric acid. Because the final bomb solution contains HCl(aq), H_2SO_4(aq), and HNO_3(aq), in the analysis, the total amount of acids has to be measured. The amount of sulfuric acid was determined by the gravimetric $BaSO_4$ method. The amount of nitric acid was determined by using Devarda's alloy method,[21] and corrections were based on −59.7 kJ·mol^{-1} for the molar formation energy of the formed 0.1 mol·dm^{-3} of aqueous HNO_3 on the basis of eq 1. The amount of hydrochloric acid in the solution was computed from the difference between the total amount of acid and the amounts of nitric acid and sulfuric acid. The extent of As_2O_3(aq) oxidation was determined by titration with a standardized iodine solution.[21] On the basis of the literature,[22] the calculation of the energetic term $\Delta U(As_2O_3)$ was equal to 1/2 of the enthalpy of reaction 2, and the standard state correction, ΔU_Σ, was calculated.

$$1/2N_2(g) + 5/4O_2(g) + 1/2H_2O(l) = HNO_3(aq) \tag{1}$$

$$As_2O_3(aq) + O_2(g) = As_2O_5(aq) \tag{2}$$

The standard molar reaction enthalpy of eq 2, $\Delta_r H_m^\theta$, was (-326.4 ± 0.4) kJ·mol^{-1}.[23] The results of the IR spectrum, XRD, and chemical and elementary analyses have shown that the final solid product was only CuO. The analytical results of the final products indicated that the combustion reaction was complete.

The energy equivalent of the calorimeter was calibrated with benzoic acid, which has an isothermal heat of combustion of $(-26\,434 \pm 3)$ J·g^{-1},[24] at 298.15 K. The calibrated experimental results have an accuracy uncertainty of $4.38 \cdot 10^{-4}$ and give an equivalence of $(18\,604.99 \pm 8.14)$ J·K^{-1} as listed in Table 3.

To measure the combustion energy for the compound involving sulfur and chlorine, the combustion energies of thianthrene and 4-chlorobenzoic acid were determined as $(-33\,507.76 \pm 14.13)$ J·g^{-1} and $(-19\,583.62 \pm 8.44)$ J·g^{-1}, respectively. The results are in good agreement with the published values $(-33\,468 \pm 4)$ J·g^{-1} [25] and $(-19\,562.08)$ J·g^{-1}.[26] For thianthrene, the precision is $4.22 \cdot 10^{-4}$, and the accuracy is $1.19 \cdot 10^{-3}$. For 4-chlorobenzoic acid, the precision is $4.31 \cdot 10^{-4}$, and the accuracy is $1.10 \cdot 10^{-3}$.

Correction of the Heat Exchange. The temperature rise must be corrected on the basis of the heat exchange between the calorimetric tube and its surroundings. The correct value of the heat exchange was calculated according to the Linio−Pyfengdelel−Wsava equation.[27]

$$\varsigma = \left(\frac{V_n - V_0}{\theta_n - \theta_0}\right)\left(\frac{T_0 + T_n}{2} + \sum_{i=1}^{n-1} T_i - n\theta_0\right) + nV_0 \tag{3}$$

where ς/K denotes the correct value of the heat exchange; n is the number of readings for the main (or reaction) period; V_n/

Table 3. Calibrated Experimental Results for the Energy Equivalent of the Calorimeter Using Benzoic Acid

	mass of benzoic acid	calibrated	calibrated heat of acid containing nitrogen	calibrated heat of combustion wire	energy equivalent of calorimeter
no.	a/g	ΔT/K	Q_N/J	q_c/J	W/J·K^{-1}
1	0.98450	1.4004	25.90	12.60	18610.95
2	0.86320	1.2301	19.96	12.60	18576.04
3	1.10295	1.5658	19.49	12.60	18640.61
4	1.11940	1.5924	25.99	12.60	18606.39
5	0.82615	1.1764	23.82	12.60	18594.75
6	0.93520	1.3317	19.31	11.70	18586.83
7	0.84385	1.1999	22.46	12.60	18619.38
$(\bar{x} \pm S_{\bar{x}})$[a]					18604.99 ±8.14

[a] $S_{\bar{x}} = [\sum_{i=1}^{n}(x_i - \bar{x})^2/n(n-1)]^{1/2}$, in which n is the experimental number; x_i is a single value obtained from a series of measurements; and $\bar{x}$ is the mean value of the results.

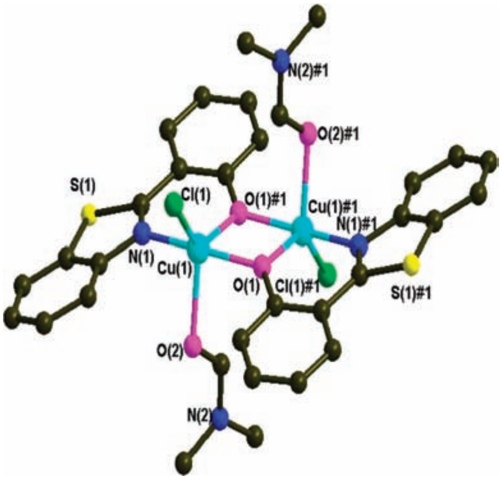

Figure 1. Single-crystal structure of $[Cu(BTZ)(DMF)Cl]_2$. The hydrogen atoms are omitted for clarity, and the others not signed are carbon atoms.

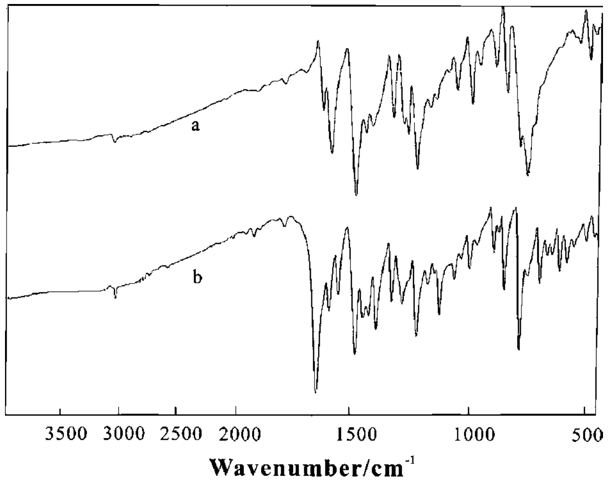

Figure 2. Comparison of IR spectrum of BTZ (a) and $[Cu(BTZ)(DMF)Cl]_2$ (b).

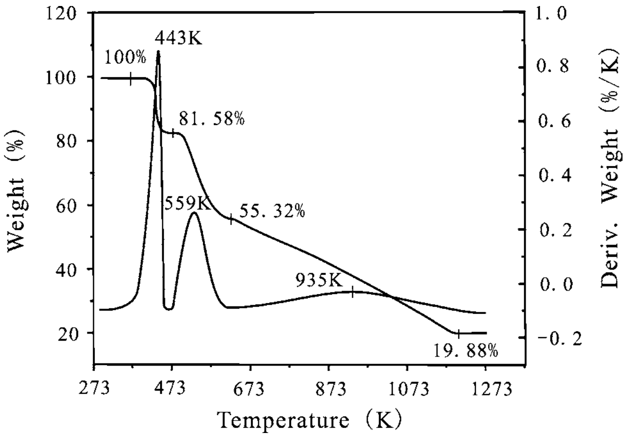

Figure 3. TG−DTG curve of $[Cu(BTZ)(DMF)Cl]_2$.

Scheme 1. Thermal Decomposed Procedure of $[Cu(BTZ)(DMF)Cl]_2$

$$[Cu(C_{13}H_8NOS)(C_3H_7NO)Cl]_2 \xrightarrow[81.58\%\ (81.65\%)]{397\sim443\sim477\text{K}} [Cu(C_{13}H_8NOS)Cl]_2$$

$$\xrightarrow[55.32\%\ (55.26\%)]{477\sim559\sim619\text{K}} Cu_2(C_{13}H_8NO_2S)Cl_2 \xrightarrow[19.88\%\ (19.94\%)]{619\sim935\sim1205\text{K}} 2CuO$$

(K·min^{-1}) and V_0/(K·min^{-1}) are the rates of temperature change at the final and initial stages, respectively (V is positive when the temperature decreases); θ_n/K and θ_0/K are the average temperatures of the calorimeter at the final and initial stages, respectively; T_0/K is the last reading of the initial stage; T_n/K is the first reading of the final stage; $\sum_{i=1}^{n-1}T_i$ is the sum of all the temperature readings except for the last one of the main period; and $(V_n - V_0)/(\theta_n - \theta_0)$ is a constant related to the calorimeter performance.

Results and Discussion

Crystal Structure. The crystal data for the title complex are: monoclinic, $a = 10.479(3)$ Å, $b = 8.993(3)$ Å, $c = 18.482(6)$ Å, $\alpha = 90°$, $\beta = 105.697(5)°$, $\gamma = 90°$, space group $P21/c$. As seen in Figure 1, the complex exists as a dimer that consists of two copper(II) ions, two BTZ, two DMF, and two chlorine ions in each independent crystallographic unit. The five-coordinate Cu^{2+} ions display distorted trigonal-bipyramidal geometry. Each Cu^{2+} ion is coordinated by three oxygen atoms from two 2-(2-hydroxyphenyl)benzothiazolate ligands [Cu(1)−O(1), 2.032(3) Å; Cu(1)−O(1)#1, 1.972(3) Å] and a DMF molecule [Cu(1)−O(2), 2.177(3) Å], respectively, one nitrogen atom from the 2-(2-hydroxyphenyl)benzothiazolate ligand [Cu(1)−N(1), 1.968(4) Å], and one chlorine ion [Cu(1)−Cl(1), 2.2495(14) Å]. In the dimer, the two Cu^{2+} ions are connected by the phenoxide oxygens and shaped into a parallelogram. A symmetry center is located in the parallelogram center. The O(1)#1−Cu(1)−Cl(1) and Cu(1)#1−O(1)−Cu(1) bond angles are 94.97(9)° and 102.22(14)°, respectively.

IR Spectrum. An IR spectrum of the title complex in the region of (4000 to 400) cm^{-1} was recorded at room temperature, as depicted in Figure 2. The IR spectrum exhibited that the ν(C−N) band which occurs at 1617 cm^{-1} in the ligand (BTZ) undergoes a shift to lower energy and appears at 1593 cm^{-1} after complexation. This suggests the coordination of nitrogen of the benzothiazolate. The band at 1402 cm^{-1}, assigned to in-plane OH-bending δ_{O-H} of the phenolic hydroxyl group in the free ligand, disappeared in the spectra of the complex. This

Table 4. Experimental Results for the Constant-Volume Combustion Energy of the Complex [Cu(BTZ)(DMF)Cl]$_2$[a]

no.	1	2	3	4	5	6
m/g	0.96511	0.98004	1.08936	0.96423	1.05968	1.04930
ΔT_{test}/K	1.1504	1.1643	1.2981	1.1487	1.2621	1.2508
ς/K	0.0292	0.0312	0.0325	0.0305	0.0318	0.0321
ΔT/K	1.1796	1.1955	1.3306	1.1792	1.2939	1.2829
W/J·K^{-1}	18604.99	18604.99	18604.99	18604.99	18604.99	18604.99
G/J·cm^{-1}	0.9	0.9	0.9	0.9	0.9	0.9
b/cm	14.0	14.0	13.0	14.0	12.0	14.0
$\Delta U(\text{HNO}_3)$/J	300.26	298.74	333.51	295.99	327.61	322.50
$\Delta U(\text{As}_2\text{O}_3)$/J	154.19	156.58	174.05	154.06	169.31	167.65
ΔU_Σ/J	45.63	48.22	51.39	46.02	50.82	50.16
Q_N/J	500.08	503.54	558.95	496.07	547.74	540.31
$-\Delta_\text{c}U$/J·g^{-1}	22208.62	22168.61	22201.25	22225.33	22190.15	22219.99

[a] $\Delta U(\text{As}_2\text{O}_3)$ is the energy correction for the oxidation of the aqueous solution of As_2O_3; $\Delta U(\text{HNO}_3)$ is the energy correction for the nitric acid formation; ΔU_Σ is the standard state correction; Q_N is the total calibrated energy except for the combustion enthalpy of Ni−Cr wire for ignition.

represents the deprotonation of the phenolic hydroxyl groups. In the title complex, the typical absorption stretching mode from ν(C−O) at 1215 cm^{-1} is shifted toward lower frequency, which clearly indicates that the ligand BTZ is bonded with the Cu^{2+} ion through the oxygen atom. Compared with the corresponding vibration peak of DMF, similarly, a red shift occurs where the stretching vibration peak of C═O (1678 cm^{-1})[28] has changed to 1647 cm^{-1}. This shift discloses that the oxygen atom of C═O from the DMF molecule is involved in the complexation. Additionally, the new absorption bands appearing at 552 cm^{-1} and 521 cm^{-1} are attributed to the ν(Cu−O) and ν(Cu−N) vibrations, respectively. All of the IR analysis results are in agreement with the X-ray diffraction analysis results.

Thermogravimetric Analysis. The thermal pattern is divided into three stages (Figure 3). In the first stage, the mass loss of 18.42 % corresponds to the loss of two DMF molecules (ca. 18.35 % for two DMFs). The second stage takes place over the temperature range of (477 to 619) K, and the mass loss percentage is 26.26 %, which is in good agreement with the percent content (26.39 %) of $\text{C}_{13}\text{H}_8\text{NS}$ in the complex. Finally, the complex is completely converted to CuO determined by the XRD technique of 19.88 % (ca. 19.94 %) at 1205 K. The decomposed procedure is postulated as Scheme 1, where the middle temperatures are the peak values in the DTG curve and the values in brackets are the calculated value of the mass residual.

Constant-Volume Combustion Energy. The method of the constant-volume combustion energy determination for the title complex was the same as that for the calibration of the calorimeter with benzoic acid. The constant-volume combustion energy of the complex was calculated by eq 4

$$-\Delta_\text{c}U = \frac{W\Delta T - Gb - Q_\text{N}}{m} \tag{4}$$

where $\Delta_\text{c}U$ (complex, s) denotes the constant-volume combustion energy of the title complex (in J·g^{-1}) and W is the energy equivalent of the rotating-bomb calorimeter (in J·K^{-1}). ΔT/K is the correct value of the temperature rise $\Delta T = \Delta T_\text{test} + \varsigma$ ($\Delta T_\text{test} = T_\text{n} - T_0$), where the ς, T_0, and T_n symbols are the same as in eq 3. G is the combustion enthalpy of the Ni−Cr wire for ignition (0.9 J·cm^{-1}), and b is the length of the actual Ni−Cr wire consumed (in cm). m is the mass (in g) of the title complex, which has been corrected from apparent mass to real mass based on the calculated density of crystal data. Q_N is the total calibrated energy except for the combustion enthalpy of the Ni−Cr wire for ignition. The constant-volume combustion energy of the complex was determined six times. The experimental result is (−22 202.32 ± 6.77) J·g^{-1} as summarized in Table 4.

Standard Molar Enthalpy of Combustion. The standard molar enthalpy of combustion of the complex, $\Delta_\text{c}H^\theta_\text{m}$ (complex, s, 298.15 K), refers to the combustion enthalpy changes of the combustion reaction (eq 5) at 298.15 K and 101.325 kPa.

$$[\text{Cu}(\text{C}_{13}\text{H}_8\text{NOS})(\text{C}_3\text{H}_7\text{NO})\text{Cl}]_2(\text{s}) + 41\text{O}_2(\text{g}) + 1418\text{H}_2\text{O}(\text{l}) = 2\text{CuO}(\text{s}) + 32\text{CO}_2(\text{g}) + 2\text{N}_2(\text{g}) + 2(\text{H}_2\text{SO}_4{\cdot}115\text{H}_2\text{O})(\text{l}) + 2(\text{HCl}{\cdot}600\text{H}_2\text{O})(\text{l}) \tag{5}$$

The standard molar enthalpy of combustion is calculated from eqs 6 and 7.

$$\Delta_\text{c}H^\theta_\text{m} = \Delta_\text{c}U + \Delta nRT \tag{6}$$

$$\Delta n = n_\text{g}(\text{products}) - n_\text{g}(\text{reactants}) \tag{7}$$

where n_g is the total amount (in mol) of gases present as products or as reactants; $R = 8.31447$ J·mol^{-1}·K^{-1}, and $T = 298.15$ K. The standard molar enthalpy of combustion, $\Delta_\text{c}H^\theta_\text{m}$, is calculated to be (−17 706.91 ± 6.77) kJ·mol^{-1}.

Standard Molar Enthalpy of Formation. The standard molar enthalpy of formation was calculated according to the thermochemical eq 8

$$\Delta_\text{f}H^\theta_\text{m}([\text{Cu}(\text{C}_{13}\text{H}_8\text{NOS})(\text{C}_3\text{H}_7\text{NO})\text{Cl}]_2, \text{s}) = 2\Delta_\text{f}H^\theta_\text{m}(\text{CuO, s}) + 32\Delta_\text{f}H^\theta_\text{m}(\text{CO}_2, \text{g}) + 12\Delta_\text{f}H^\theta_\text{m}(\text{H}_2\text{O, l}) + 2\Delta_\text{f}H^\theta_\text{m}(\text{H}_2\text{SO}_4{\cdot}115\text{H}_2\text{O, l}) + 2(\text{HCl}{\cdot}600\text{H}_2\text{O, l}) - \Delta_\text{c}H^\theta_\text{m}([\text{Cu}(\text{C}_{13}\text{H}_8\text{NOS})(\text{C}_3\text{H}_7\text{NO})\text{Cl}]_2, \text{s}) \tag{8}$$

The standard molar enthalpies of formation are: CuO(s), $\Delta_\text{f}H^\theta_\text{m}$(CuO, s) = −157.3 kJ·mol^{-1};[29] CO$_2$(g), $\Delta_\text{f}H^\theta_\text{m}$(CO$_2$, g) = (−393.51 ± 0.13) kJ·mol^{-1};[29] H$_2$O (l), $\Delta_\text{f}H^\theta_\text{m}$(H$_2$O, l) = (−285.830 ± 0.040) kJ·mol^{-1};[29] HCl·600H$_2$O(l), $\Delta_\text{f}H^\theta_\text{m}$(HCl·600H$_2$O, l) = (−166.540 ± 0.005) kJ·mol^{-1};[29,30] and H$_2$SO$_4$·115H$_2$O(l), $\Delta_\text{f}H^\theta_\text{m}$ (H$_2$SO$_4$·115H$_2$O, l) = (−887.81 ± 0.01) kJ·mol^{-1}.[29,30] The result of the calculation about $\Delta_\text{f}H^\theta_\text{m}$ is (−738.67 ± 7.96) kJ·mol^{-1}.

Conclusions

A new complex, [Cu(BTZ)(DMF)Cl]$_2$, was prepared successfully and characterized by IR spectrum, TG−DTG techniques, and single-crystal X-ray diffraction. The constant-volume combustion energy of the title complex, $\Delta_\text{c}U$, has been determined as being (−17 689.56 ± 6.77) kJ·mol^{-1} by a precision rotating-bomb combustion calorimeter at 298.15 K. The standard molar enthalpy of formation of the complex, $\Delta_\text{f}H^\theta_\text{m}$, has been calculated to be (−738.67 ± 7.96) kJ·mol^{-1}. These thermochemical data can provide a theoretical basis for study of the biological activity and other properties of the title complex.

Acknowledgment

The authors are grateful to Prof. Sanping Chen (College of Chemistry and Materials Science, Northwest University, PR China)

for his constant encouragement during the course of the study. Crystallographic data for the title complex has been deposited at the Cambridge Crystallographic Data Centre as supplementary publications (CCDC 719688). These data can be obtained free of charge at www.ccdc.cam.ac.uk or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K. (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk).

Literature Cited

(1) Nicolaides, A.; Rauk, A.; Glukhovtsev, M. N.; Radom, L. Heats of Formation from G_2, $G_2(MP_2)$, and $G_2(MP_2$, SVP) Total Energies. *J. Phys. Chem.* **1996**, *100*, 17460–17464.

(2) Aleixo, A. I.; Oliveira, P. H.; Diogo, H. P.; Minas da Piedade, M. E. Enthalpies of formation and lattice enthalpies of alkaline metal acetates. *Thermochim. Acta* **2005**, *428*, 131–136.

(3) Verevkin, S. P. Thermochemical Properties of Diphenylalkanes. *J. Chem. Eng. Data* **1999**, *44*, 175–179.

(4) Ribeiro da Silva, M. A. V.; Amaral, Luísa, M. P. F.; Ferreira, A. I. M. C. L. Standard Molar Enthalpies of Formation of some Trichloroanilines by Rotating-bomb Calorimetry. *J. Chem. Thermodyn.* **2002**, *34*, 119–127.

(5) Chen, S. P.; Meng, X. X.; Xie, G.; Gao, S. L.; Shi, Q. Z. Thermochemistry of the Ternary Solid Complex $Er(C_5H_8NS_2)_3(C_{12}H_8N_2)$. *J. Chem. Eng. Data* **2005**, *50*, 1204–1211.

(6) Morais, V. M. F.; Miranda, M. S.; Matos, M.; Agostinha, R. Thermochemical Parameters of the Chloronitrophenol Isomers: A Combined Experimental and Theoretical Investigation. *J. Chem. Eng. Data* **2007**, *52*, 627–634.

(7) Dong, J. X.; Qi, Z. D.; Zhang, Z. H.; Liu, Y. Standard Molar Enthalpies of Formation and Thermal Stabilities of Artemisinin and Its Two Derivatives: Artemether and Artesunate. *J. Chem. Eng. Data* **2007**, *52*, 1045–1049.

(8) Wang, L. J.; Liu, F.; Yang, X. W.; Wang, X. Y.; Liu, R. P.; Zhao, S.; Chen, S. P. Thermochemical properties of the rare earth complexes with pyromellitic acid. *Thermochim. Acta* **2009**, *490*, 43–46.

(9) Maheswari, P. U.; van der Ster, M.; Smulders, S.; Barends, S.; van Wezel, G. P.; Massera, C.; Roy, S.; den Dulk, H.; Gamez, P.; Reedijk, J. Structure, Cytotoxicity, and DNA-Cleavage Properties of the Complex $[Cu^{II}(pbt)Br_2]$. *Inorg. Chem.* **2008**, *47*, 3719–3727.

(10) Haneda, S.; Gan, Z. B.; Eda, K.; Hayashi, M. Ligand Effects of 2-(2-Pyridyl)benzazole-Pd Complexes on the X-ray Crystallographic Structures, 1H NMR Spectra, and Catalytic Activities in Mizoroki-Heck Reactions. *Organometallics* **2007**, *26*, 6551–6555.

(11) Roh, S.-G.; Kim, Y.-H.; Seo, K. D.; Lee, D. H.; Kim, H. K.; Park, Y.-II; Park, J.-W.; Lee, J.-H. Synthesis, Photophysical, and Electroluminescent Device Properties of Zn(II)-Chelated Complexes Based on Functionalized Benzothiazole Derivatives. *Adv. Funct. Mater.* **2009**, *19*, 1663–1671.

(12) Theriot, L. J.; Lee, C. C.; Syamal, A. Oxovanadium(IV) Complexes with Tridentate ONS Donor Ligands. *Inorg. Chem.* **1971**, *10*, 1669–1673.

(13) Yu, G.; Yin, S. W.; Liu, Y. Q.; Shuai, Z. G.; Zhu, D. B. Structures, Electronic States, and Electroluminescent Properties of a Zinc(II) 2-(2 Hydroxyphenyl)benzothiazolate Complex. *J. Am. Chem. Soc.* **2003**, *125*, 14816–14824.

(14) Tong, Y. P.; Zheng, S. L.; Chen, X. M. Syntheses, Structures, Photoluminescence, and Theoretical Studies of a Class of Beryllium(II) Compounds of Aromatic N,O-Chelate Ligands. *Inorg. Chem.* **2005**, *44*, 4270–4275.

(15) Yang, Y. T.; Geng, H.; Shuai, Z. G.; Peng, J. B. First-principles electronic structure of light-emitting and transport materials: Zinc(II)2-(2-hydroxyphenyl)benzothiazolate. *Synth. Met.* **2006**, *156*, 1287–1291.

(16) Zhu, F. J.; Hua, Y. L.; Yin, S. G.; Deng, J. C.; Wu, K. W.; Niu, X.; Wu, X. M.; Petty, M. C. Effect of the thickness of $Zn(BTZ)_2$ emitting layer on the electroluminescent spectra of white organic light-emitting diodes. *J. Lumin.* **2007**, *122−123*, 717–719.

(17) Xu, B. S.; Xu, H. X.; Fang, X. H.; Chen, L. Q.; Wang, H.; Liu, X. G. Structure, Charge-Transfer and Luminescent Properties of Bis(2-(2-hydroxyphenyl)benzothiazolate)beryllium. *Org. Electron.* **2008**, *9*, 906–910.

(18) Hamada, Y.; Sano, T.; Fujii, H.; Nishio, Y.; Takahashi, H.; Shibata, K. White-Light-Emitting Material for Organic Electroluminescent Devices. *Jpn. J. Appl. Phys.* **1996**, *35*, 1339–1341.

(19) Sheldrick, G. M. *SHELXT 97, Program for Crystal Structure Refinement*; University of Göttingen: Germany, 1997.

(20) Yang, X. W.; Chen, S. P.; Gao, S. L. Construction of a Rotating-bomb Combustion Calorimeter and Measurement of Thermal Effects. *Instrum. Sci. Technol.* **2002**, *30*, 311–321.

(21) Vogel, A. I. *Quantitative Inorganic Analysis*; Longman: London, 1978.

(22) Hubbard, W. N.; Scott, D. W.; Waddington, G. *Experimental thermochemistry*; Interscience Publishers Inc.: New York, 1956; pp 75−128.

(23) Bjellerup, L.; Sunner, S.; Wadsö, I. *Acta Chem. Scand.* **1957**, *11*, 1761–1765.

(24) *Certificate of Analysis of Standard Reference Material 39i-Benzoic Acid*; National Institute of Standards and Technology: Gaithersburg, 1995.

(25) Johnson, W. H. The Enthalpies of Combustion and Formation of Thianthrene. *J. Res. Natl. Bur. Stand.* **1975**, *79*, 561.

(26) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermodynamic Data of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986.

(27) Popov, M. M. *Thermometry and Calorimetry*; Moscow University Publishing House: Moscow, 1954; p 382.

(28) Wang, J. P.; Wu, Q.; Niu, J. Y. A Novel One-dimensional Organic-inorganic Polymer: Synthesis and Crystal Structure of $[\{Ca(DMF)_5\}_2SiMo_{12}O_{40}]_n$. *Sci. China Ser. B: Chem.* **2002**, *45*, 647–654.

(29) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere Publishing Corp: New York, 1989.

(30) The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Data* **1982**, *11* (Suppl. 2).

Received for review August 1, 2009. Accepted January 15, 2010. The author are thankful for the financial support of the Education Committee of Shaanxi Province (Grant No. 05JC31) and “13115” S&T innovation program of Shaanxi province (No. 2008ZDKG-22).

JE900651U