Thermal Decomposition Procedures and Thermodynamic Properties of Some Transition Metal Complexes with 2-(2-Hydroxyphenyl)Benzothiazolate

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Five complexes of $M(BTZ)_2$ [M = Mn, Co, Ni, Cu, Zn; BTZ = 2-(2-hydroxyphenyl)benzothiazolate] were synthesized by the reaction of hydrated metal chloride with the ligand BTZ in the mixed solvent of ethanol and methanol and characterized by chemical and elemental analysis, IR spectroscopy, and thermogravimetric/differential thermogravimetric analysis (TG-DTG). The results show that their thermal decomposition temperature was over 573 K and the complexes were completely converted to oxides at higher temperature. In addition, the constant-volume combustion energies of the complexes, $\Delta_c U$, were determined by a precise rotating-bomb calorimeter (RBC-type II). Their standard molar enthalpies of combustion, $\Delta_c H_m^\theta$, and standard molar enthalpies of formation, $\Delta_f H_m^\theta$, were calculated at 298.15 K. The values of standard molar enthalpies of formation were derived and range between [−(339.97 ± 6.09) and −(2165.92 ± 5.91)] $kJ \cdot mol^{-1}$ for the complexes.

Introduction

Over the past two decades, the complexation of metal cations with the 2-(2-hydroxyphenyl)benzothiazolate (BTZ) ligand has been extensively explored. Some new transition metal oxocomplexes, such as oxorhenium(V) and oxotechnetium(V), formed from the bidentate BTZ ligand with N and O donors, have been recently gained considerable attention.[1−3] Because of its excellent electroluminescence properties, $Zn(BTZ)_2$ has become a new effective white-light emitting material used in organic light-emitting diodes (OLEDs). Studies on the complexes $Zn(BTZ)_2$ have been reported by many different authors from the theoretical calculation of electronic characteristics, crystal structure, and device performance.[4−7] Additionally, scientific workers have found that $Be(BTZ)_2$ displays strong photoluminescence in the blue region that can serve as a candidate for an electron-transport material.[8,9]

The successful use of these materials in technical processes requires knowledge of their thermodynamic stability. A set of thermodynamic data may enable material scientists to select BTZ complexes for specific technological applications. However, no systematic investigation of their thermal decomposition and thermodynamic properties has been made up to now.

The aim of the present work is to systematically study BTZ complexes associated with the first transition period metal ions. As part of this work, very recently, we reported the synthesis, crystal structure, and thermochemical properties of a new complex $[Cu(BTZ)(DMF)Cl]_2$.[10] Here we have synthesized and characterized another five metal complexes of the BTZ ligand. Their constant-volume combustion energies, $\Delta_c U$, were determined by a precise rotating-bomb calorimeter (RBC-type II). From the constant-volume combustion energies, some thermodynamic parameters such as the standard molar enthalpies of combustion, $\Delta_c H_m^\theta$, and the standard molar enthalpies of formation, $\Delta_f H_m^\theta$, of the complexes in the solid state were derived at 298.15 K. Meanwhile, the thermal decomposition behavior were deduced using the thermogravimetric/differential thermogravimetric analysis (TG-DTG) technique, and the results indicated that their thermal decomposition temperature was over 573 K. The data obtained in this work may be useful and helpful for the further application of these complexes.

Experimental Section

Materials and Analysis Methods. The ligand BTZ was synthesized according to a literature method.[11] The determined value of the melting point was (403 to 404) K, which is in agreement with the reference value. Benzoic acid was purchased from the Shanghai Reagent Company, with a mass fraction purity of 0.99999, and dried in a vacuum oven prior to use. Other reagents were of analytical grade and used without any further purification.

Elemental analysis (C, H, and N) was performed by a Vario EL III elemental analyzer (Germany). The amount of Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} were determined with EDTA by complexometric titration, and Cu^{2+} was determined by iodimetry. IR spectra (KBr pellet) were recorded with a model Equinox55 FT-IR spectrophotometer (Bruker, Germany, the resolution was ± 4 cm^{-1}). The TG-DTG experiment of the complexes was performed using a Perkin-Elmer thermogravimetric instrument under a static air atmosphere. The heating rate used was 10 $K \cdot min^{-1}$ from ambient temperature to 1273 K.

Preparation of the Complexes. BTZ (0.03 mol) was dissolved in 30 mL mixed sodium hydroxide solution of ethanol and methanol (1:1 volume ratio). The molar ratio of BTZ and sodium hydroxide is 1:1. $MCl_2 \cdot nH_2O$ salts (M = Mn, $n = 4$; M = Co, Ni, $n = 6$; M = Cu, $n = 2$; M = Zn, $n = 0$) were dissolved in a mixed solvent of ethanol and methanol (30 mL), and the solution of $MCl_2 \cdot nH_2O$ was added dropwise into the solution of BTZ under electromagnetic stirring. After the reaction lasted for 2 h at room temperature, the precipitates were filtered, washed with distilled water and ethanol repeatedly, and dried in a vacuum desiccator over P_4O_{10}.

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Table 1. Analytical Results Related to the Composition of the Complexes

complex	*w* (found)/% (*w* (calculated)/%) M	C	H	N	yield/%
$\mathrm{Mn(BTZ)_2}$	10.79 (10.83)	61.48 (61.53)	3.15 (3.18)	5.51 (5.52)	86
$\mathrm{Co(BTZ)_2}$	11.47 (11.52)	61.11 (61.05)	3.08 (3.15)	5.41 (5.48)	88
$\mathrm{Ni(BTZ)_2}$	11.53 (11.48)	61.05 (61.08)	3.19 (3.15)	5.44 (5.48)	89
$\mathrm{Cu(BTZ)_2}$	12.37 (12.31)	60.56 (60.51)	3.08 (3.12)	5.50 (5.43)	88
$\mathrm{Zn(BTZ)_2}$	12.60 (12.63)	61.25 (60.29)	3.05 (3.11)	5.37 (5.41)	85

Table 2. Data of IR Spectra of Main Groups of BTZ and Complexes ($\mathrm{cm^{-1}}$)

compounds	ν(C−N)	ν(C−O)	(O−H)	ν(C=C)	ν(M−O or M−N)
BTZ	1617	1215	1402	1584 1482 1432	
$\mathrm{Mn(BTZ)_2}$	1596	1202		1548 1489 1471 1420	635 586 551 516
$\mathrm{Co(BTZ)_2}$	1597	1203		1548 1491 1469 1421	634 585 551 517
$\mathrm{Ni(BTZ)_2}$	1596	1202		1548 1491 1469 1421	633 585 551 516
$\mathrm{Cu(BTZ)_2}$	1599	1203		1546 1488 1468 1420	634 583 550 516
$\mathrm{Zn(BTZ)_2}$	1601	1205		1541 1487 1470 1419	634 581 550 515

Apparatus and Conditions of the Calorimetric Experiment. The constant-volume combustion energies of the complexes were determined with a precise rotating-bomb calorimeter (RBC-type II). The main experimental procedures were described previously.[12] 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. 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.[10,13]

The energy equivalent of the calorimeter was calibrated with benzoic acid, which has an isothermal heat of combustion of $(-26434 \pm 3)\ \mathrm{J\cdot g^{-1}}$[14] at 298.15 K. The calibrated experimental results have an uncertainty of $4.38\cdot 10^{-4}$ and give an equivalence of $(18604.99 \pm 8.14)\ \mathrm{kJ\cdot K^{-1}}$.

The analytical methods of the final products (gas, liquid, and solid) were as reported in ref 12. 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. The amount of sulfuric acid was determined by the gravimetric $\mathrm{BaSO_4}$ method. The amount of nitric acid was determined by using Devarda's alloy method.[15] Because the crucible in the rotating bomb was attached to the support, the final solid products were left in the crucible at the end of the experiment. Analytical data of the final products indicate that the combustion reaction was complete. The final products were shown to be MO (except for $\mathrm{MnO_2}$) by IR spectroscopy, X-ray diffraction (XRD), and chemical and elemental analysis.

To measure the energy of combustion for the compound involving sulfur, the energy of combustion of thianthrene was determined as $(-33507.76 \pm 14.13)\ \mathrm{J\cdot g^{-1}}$. The precision is $4.22\cdot 10^{-4}$, and the accuracy is $1.19\cdot 10^{-3}$, which is in good agreement with the published value of $(-33468 \pm 4)\ \mathrm{J\cdot g^{-1}}$.[16]

The relative atomic masses used in the calculation of all molar quantities were those recommended by the IUPAC Commission in 2005.[17]

Results and Discussion

Chemical and Elemental Analysis of Complexes. The yields and chemical and elemental analytical results of the composition of the complexes are shown in Table 1. On the basis of the data, the composition of these complexes can be identified with the general formula $\mathrm{M(BTZ)_2}$ ($\mathrm{BTZ = C_{13}H_8NOS^-}$).

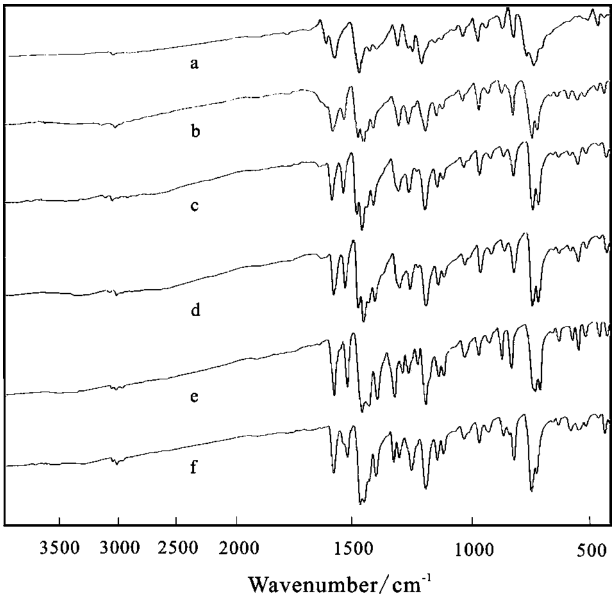

Figure 1. IR spectra of the BTZ (a), $\mathrm{Mn(BTZ)_2}$ (b), $\mathrm{Co(BTZ)_2}$ (c), $\mathrm{Ni(BTZ)_2}$ (d), $\mathrm{Cu(BTZ)_2}$ (e), and $\mathrm{Zn(BTZ)_2}$ (f).

IR Spectra. IR spectra of the complexes in the region of (4000 to 400) $\mathrm{cm^{-1}}$ were recorded at room temperature, as depicted in Figure 1. The spectra of the complexes are quite similar because of their similar structure. Vibration characteristic absorptions of the main groups of the BTZ, and its complexes are listed in Table 2. Take the complex $\mathrm{Ni(BTZ)_2}$, for example; the ν(C−N) band which occurs at 1617 $\mathrm{cm^{-1}}$ in the ligand undergoes a shift to lower energy and appears at (1596 to 1601) $\mathrm{cm^{-1}}$ after complexation, which suggests the coordination of the nitrogen of the benzothiazolate. In the complex $\mathrm{Ni(BTZ)_2}$, the typical absorption stretching mode from ν(C−O) at 1215 $\mathrm{cm^{-1}}$ is shifted toward lower frequency, and the intensity has increased marginally, which clearly indicates that the ligand is bonded with metal ions through the oxygen atom. The band at 1402 $\mathrm{cm^{-1}}$, assigned to in-plane OH-bending $\delta_{\mathrm{O-H}}$ of the phenolic hydroxyl groups in the free ligand, disappeared in the spectra of the complex $\mathrm{Ni(BTZ)_2}$. This represents the deprotonation of phenolic hydroxyl groups. Compared to the spectrum of BTZ, a red shift occurs in the stretching vibration peak of C=C [(1584, 1482, and 1432) $\mathrm{cm^{-1}}$] that has changed to (1548, 1491, 1469, and 1421) $\mathrm{cm^{-1}}$. Additionally, the new absorption bands appearing at (633, 585, 551, and 516) $\mathrm{cm^{-1}}$ are attributed to the ν(Ni−O) or ν(Ni−N) vibrations. From the above data, it can be concluded that the ligand BTZ and metal ions formed

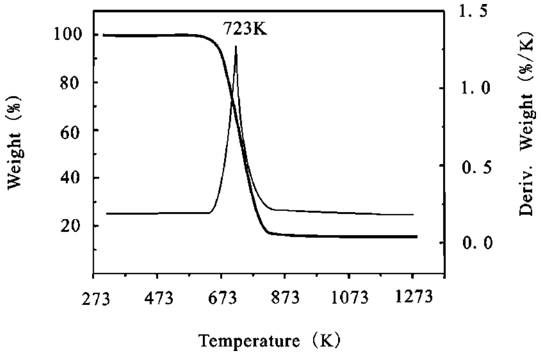

Figure 2. TG-DTG curve of the complex $Mn(BTZ)_2$.

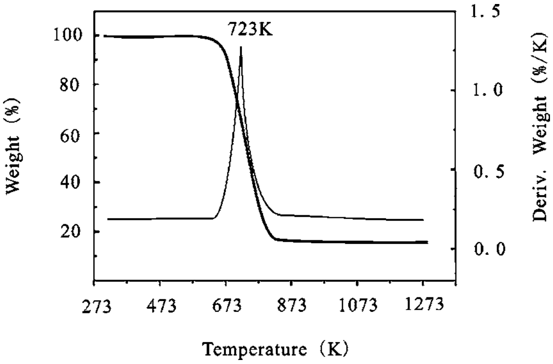

Figure 3. TG-DTG curve of the complex $Co(BTZ)_2$.

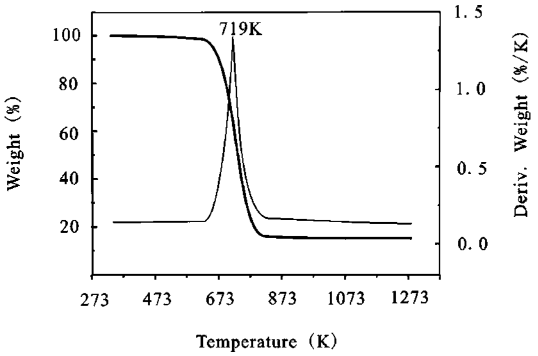

Figure 4. TG-DTG curve of the complex $Ni(BTZ)_2$.

complexes via both the deprotonated phenolic hydroxyl and the heterocyclic nitrogen atom of the benzothiazole.

TG-DTG. The thermal decomposition behaviors of transition metal complexes with BTZ were investigated by a TG-DTG technique and are presented in Figures 2 to 6. The TG-DTG curves indicated that all of the complexes experienced a similar stage of weight loss, and the thermal decomposition occurred in one stage between (581 and 885) K. An example of $Ni(BTZ)_2$ is demonstrated. The stage began at about 618 K and was completed at 818 K with a weight loss of 83.86 % (the calculated loss weight was 83.82 %). The final weight corresponded to Ni_2O_3 determined by an XRD technique. The decomposition 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 values of the mass residual. The residue of transition metal complexes with BTZ is presented in Table 3.

Combustion Energies of Complexes. The constant-volume combustion energies of the complexes were measured by six experiments. The methods of determination used were similar to that for benzoic acid. The values were calculated by eq 2

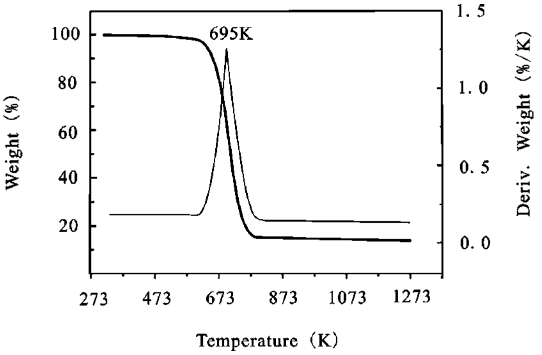

Figure 5. TG-DTG curve of the complex $Cu(BTZ)_2$.

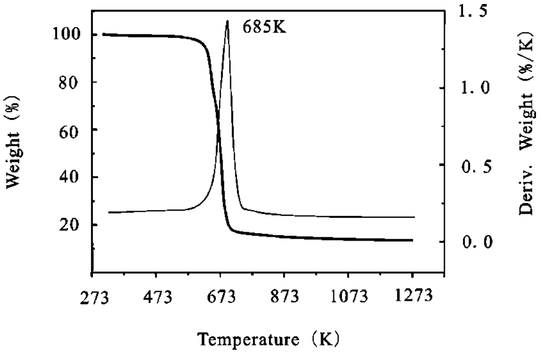

Figure 6. TG-DTG curve of the complex $Zn(BTZ)_2$.

Table 3. TG-DTG Data of the Complexes

		residue (%)[a]	
complexes	temperature range (K)	found	calculated
$Mn(BTZ)_2$	642 to 761 to 885	15.49	15.55
$Co(BTZ)_2$	627 to 723 to 825	16.17	16.22
$Ni(BTZ)_2$	618 to 719 to 818	16.14	16.18
$Cu(BTZ)_2$	594 to 695 to 785	15.33	15.41
$Zn(BTZ)_2$	581 to 685 to 734	15.68	15.72

[a] The final decomposition products are $(1/2)M_2O_3$ (M = Mn, Co, Ni) and MO (M = Cu, Zn).

Scheme 1. Thermal Decomposition Reaction of $Ni(BTZ)_2$ Complex

$$Ni(BTZ)_2 \xrightarrow[16.14\%\ (16.18\%)]{618\text{-}719\text{-}818\ K} \frac{1}{2}\ Ni_2O_3$$

$$-\Delta_c U = \frac{W\Delta T - Gb - Q_N}{m} \qquad (2)$$

where $\Delta_c U$ (complexes, s) denotes the constant-volume combustion energy of the complexes (in $J \cdot g^{-1}$), W the energy equivalent of the rotating-bomb calorimeter (in $J \cdot K^{-1}$), m is the mass (in g) of the complex, and b is the length of the actual Ni–Cr wire consumed (in cm). G is the combustion enthalpy of Ni–Cr wire for ignition ($0.9\ J \cdot cm^{-1}$), Q_N is the total calibrated energy except for the combustion enthalpy of Ni–Cr wire for ignition, and ΔT is the correct value of the temperature rise. The experimental results are summarized in Table 4.

Standard Molar Enthalpies of Combustion and Formation of Complexes. The standard molar enthalpies of combustion of the complexes, $\Delta_c H_m^\theta$, refer to the combustion enthalpy changes combustion reaction (eqs 3 and 4) at 298.15 K and 101.325 kPa.

Table 4. Constant-Volume Combustion Energies of the Complexes

complex	no.	mass of complexes, m	calibrate value of the temperature rise, νT	the total calibrated heat, Q_N	calibrated heat of combustion wire, q_c	constant-volume combustion energy, $-\Delta_c U$
		g	K	J	J	$J \cdot g^{-1}$
$Mn(BTZ)_2$	1	0.72185	1.0132	192.25	12.60	25830.47
	2	0.70110	0.9829	187.37	11.70	25799.14
	3	0.70655	0.9912	188.66	11.70	25816.87
	4	0.71025	0.9954	189.52	12.60	25789.91
	5	0.71445	1.0003	190.51	10.80	25767.04
	6	0.70973	0.9943	189.40	12.60	25780.14
	$(\bar{x} \pm S_{\bar{x}})^a$					25797.26 ± 9.58
$Co(BTZ)_2$	1	0.66235	0.9584	177.04	12.60	26634.53
	2	0.67740	0.9788	180.55	11.70	26599.22
	3	0.66985	0.9681	178.78	12.60	26603.14
	4	0.65825	0.9505	176.08	12.60	26578.60
	5	0.65995	0.9545	176.48	12.60	26622.29
	6	0.66345	0.9577	177.29	11.70	26571.72
	$\bar{x} \pm S_{\bar{x}}$					26601.58 ± 9.90
$Ni(BTZ)_2$	1	0.81240	1.1230	212.16	12.60	25441.46
	2	0.80675	1.1148	210.84	12.60	25432.17
	3	0.79430	1.0971	207.98	11.70	25420.94
	4	0.78960	1.0892	206.83	12.60	25386.43
	5	0.81555	1.1254	212.89	12.60	25397.05
	6	0.82075	1.1352	214.15	12.60	25456.76
	$\bar{x} \pm S_{\bar{x}}$					25422.47 ± 10.92
$Cu(BTZ)_2$	1	0.73675	1.0093	192.77	12.60	25208.89
	2	0.74830	1.0256	195.44	11.70	25222.69
	3	0.73445	1.0086	192.23	12.60	25270.83
	4	0.74296	1.0186	194.21	12.60	25229.13
	5	0.72115	0.9891	189.16	12.60	25238.07
	6	0.74645	1.0245	195.01	12.60	25257.15
	$\bar{x} \pm S_{\bar{x}}$					25237.79 ± 9.32
$Zn(BTZ)_2$	1	0.72690	0.9079	189.98	10.80	22961.47
	2	0.72105	0.8992	188.63	11.70	22923.90
	3	0.75235	0.9403	195.84	12.60	22975.79
	4	0.76210	0.9507	198.09	12.60	22932.78
	5	0.72315	0.9036	189.11	12.60	22968.62
	6	0.73425	0.9178	191.67	12.60	22977.72
	$\bar{x} \pm S_{\bar{x}}$					22956.71 ± 9.34

[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.

Table 5. Constant-Volume Combustion Energies, Standard Molar Enthalpies of Combustion, and Standard Molar Enthalpies of Formation for the Complexes

complexes	$-\Delta_c U$	$-\Delta_c H_m^\theta$	$-\Delta_f H_m^\theta$
	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
$Mn(BTZ)_2$	13091.75 ± 4.86	13106.62 ± 4.86	1145.27 ± 5.93
$Co(BTZ)_2$	13606.20 ± 5.06	13619.83 ± 5.06	339.97 ± 6.09
$Ni(BTZ)_2$	12997.01 ± 5.58	13010.64 ± 5.58	950.92 ± 6.53
$Cu(BTZ)_2$	13025.07 ± 4.81	13038.70 ± 4.81	840.46 ± 5.88
$Zn(BTZ)_2$	11890.59 ± 4.84	11904.22 ± 4.84	2165.92 ± 5.91

$$Mn(C_{13}H_8NOS)_2(s) + 33O_2(g) + 224H_2O(l) = MnO_2(s) + 26CO_2(g) + N_2(g) + 2(H_2SO_4 \cdot 115H_2O)(l) \quad (3)$$

$$M(C_{13}H_8NOS)_2(s) + \frac{65}{2}O_2(g) + 224H_2O(l) = MO(s) + 26CO_2(g) + N_2(g) + 2(H_2SO_4 \cdot 115H_2O)(l) \quad (4)$$

$$(M = Ni, Co, Cu, and Zn)$$

The standard molar enthalpies of combustion of the complexes are calculated by eqs 5 and 6.

$$\Delta_c H_m^\theta = \Delta_c U + \Delta nRT \quad (5)$$

$$\Delta n = n_g(\text{products}) - n_g(\text{reactants}) \quad (6)$$

where n_g is the total amount (in mol) of gases present as products or as reactants, $R = 8.314\ J \cdot mol^{-1} \cdot K^{-1}$, and $T = 298.15$ K. The results of the calculation are given in Table 5.

The standard molar enthalpies of formation of the complexes, $\Delta_f H_m^\theta$, are calculated by Hess's law according to the thermochemical eq 7.

$$\Delta_f H_m^\theta(M(BTZ)_2, s) = \Delta_f H_m^\theta(MO_n, s) + 26\Delta_f H_m^\theta(CO_2, g) + 6\Delta_f H_m^\theta(H_2O, l) + 2\Delta_f H_m^\theta(H_2SO_4 \cdot 115H_2O) - \Delta_c H_m^\theta(M(BTZ)_{2,}s) \quad (7)$$

$$(M = Mn, n = 2; M = Ni, Co, Cu, and Zn, n = 1)$$

The standard molar enthalpies of formation are: $MnO_2(s)$, $\Delta_f H_m^\theta(MnO_2, s) = -530.03\ kJ \cdot mol^{-1}$;[18] CoO(s), $\Delta_f H_m^\theta(CoO, s) = -237.94\ kJ \cdot mol^{-1}$;[18] NiO(s), $\Delta_f H_m^\theta(NiO, s) = -239.70\ kJ \cdot mol^{-1}$;[18] CuO(s), $\Delta_f H_m^\theta(CuO, s) = -157.30\ kJ \cdot mol^{-1}$;[18] ZnO(s), $\Delta_f H_m^\theta(ZnO, s) = -348.28\ kJ \cdot mol^{-1}$;[18] $CO_2(g)$, $\Delta_f H_m^\theta(CO_2, g) = (-393.51 \pm 0.13)\ kJ \cdot mol^{-1}$;[18] $H_2O(l)$, $\Delta_f H_m^\theta(H_2O, l) = (-285.830 \pm 0.042)\ kJ \cdot mol^{-1}$[18] and $H_2SO_4 \cdot 115H_2O$ (l), $\Delta_f H_m^\theta(H_2SO_4 \cdot 115H_2O, l) = (-887.81 \pm 0.01)\ kJ \cdot mol^{-1}$.[18,19] The results of the calculations are also listed in Table 5.

Summary

Five members of first transition period metal complexes with the BTZ ligand were successfully prepared and characterized by IR spectroscopy. It is indicated that these complexes have a similar coordination mode, and the nitrogen and oxygen atoms from the BTZ ligand coordinated to M^{2+} in a bidentate fashion. The results of TG-DTG exhibit all of the obtained BTZ complexes decomposed with one stage, and the thermal decomposition temperature was over 573 K. The constant-volume combustion energies of the complexes, $\Delta_c U$, have been determined by a precision rotating-bomb combustion calorimeter at 298.15 K. The standard molar enthalpies of formation of the complexes, $\Delta_f H_m^\theta$, have been calculated. These data may be useful for the further application of these complexes.

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