Thermochimica Acta 506 (2010) 41–46

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Low-temperature heat capacities and thermodynamic properties of ethylenediammonium tetrachlorozincate chloride $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$

Dong-Hua He [a], You-Ying Di [a,*], Bin Wang [a], Wen-Yan Dan [a], Zhi-Cheng Tan [b]

[a] College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, Shandong Province, PR China
[b] Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning Province, PR China

ARTICLE INFO

Article history:
Received 27 January 2010
Received in revised form 14 April 2010
Accepted 21 April 2010
Available online 23 May 2010

Keywords:
Ethylenediammonium tetrachlorozincate chloride
X-ray crystallography
Low-temperature heat capacity
Isoperibol solution-reaction calorimetry
Standard molar enthalpy of formation

ABSTRACT

The ethylenediammonium tetrachlorozincate chloride $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$ was synthesized. Chemical analysis, elemental analysis, and X-ray crystallography were applied to characterize the composition and crystal structure of the complex. Low-temperature heat capacities of the compound were measured by a precision automatic adiabatic calorimeter over the temperature range from $T = 77$–377 K. A polynomial equation of heat capacities as a function of the reduced temperature was fitted by a least square method. Based on the polynomial equation, the smoothed heat capacities and thermodynamic functions of the title compound relative to the standard reference temperature 298.15 K were calculated at intervals of 5 K. A thermochemical cycle was designed and the enthalpy change of the solid phase reaction of ethylenediamine dihydrochloride with zinc chloride was determined to be $\Delta_r H_m^\circ = -(17.9 \pm 0.6)\,\mathrm{kJ\,mol^{-1}}$ by an isoperibol solution-reaction calorimeter. Finally, the standard molar enthalpy of formation of the title compound was derived to be $\Delta_f H_m^\circ[(C_2H_{10}N_2)_2(ZnCl_4)Cl_2, s] = -(1514.4 \pm 2.7)\,\mathrm{kJ\,mol^{-1}}$ in accordance with Hess law.

1. Introduction

In recent years, the design and synthesis of organic–inorganic hybrid materials have aroused great interest [1]. By means of the reaction of a variety of inorganic metal chlorides with organic conjugated molecules, short-chain oligomerics, long-chain molecules, and long chain polymers, many materials with low-dimensional and perovskite structure were synthesized and their optical, electrical, and magnetic properties were studied [2]. Organic components in this kind of the complex can not only be used as a template, but also may as an activated layer to modify the electro-optical nature of quantum well through introducing functional groups [3]. Hybrid compounds formed by organic amine and inorganic divalent metal chloride have many practical and potential applications in various fields, such as unusual topological properties and potential applications in the fields of catalysis, biochemistry, and magnetism material science [4]. It is important to investigate deeply the relationship between the perovskite structure and functional properties of the hybrid compound, which is an basis for design and development of the materials with unique capabilities [3]. Thermodynamic properties of the complex $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$ as one of organic–inorganic hybrid materials have not been reported in the literature, which is needed for the purpose of development of new application fields and relevant theoretical research. In this paper, the title complex was synthesized. X-ray crystallography was used to characterize the crystal structure of the compound. Molar heat capacities were measured by an adiabatic calorimeter over the temperature range from 77 to 377 K. The smoothed heat capacities and the various thermodynamic functions relative to 298.15 K have been calculated based on the fitted polynomial equation through numerical integration. Finally, the standard molar enthalpy of formation of the title compound $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2(s)$ was determined by an isoperibol solution-reaction calorimeter.

2. Experimental

2.1. Synthesis and characterization of the sample

All chemicals including ethylenediamine, zinc chloride, concentrated hydrochloric acid, and anhydrous ethanol used in the experiments were of analytical grade. The reactants were accurately weighed at the molar ratio of $n(NH_2CH_2CH_2NH_2):n(ZnCl_2):n(HCl) = 2:1:4$ based on the stoichiometric coefficient of the reaction. The weighed samples were slowly mixed in anhydrous ethanol and refluxed for 4 h under boiling. The final mixed solution was cooled naturally to room temperature and filtered. The filter cake was washed three times

* Corresponding author. Fax: +86 635 8239121.
E-mail addresses: diyouying@126.com, yydi@lcu.edu.cn (Y.-Y. Di).

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doi:10.1016/j.tca.2010.04.012

with anhydrous ethanol, dissolved in double distilled water, and laid aside. Several days later, a colourless transparent crystal suitable for single crystal diffraction analysis appeared. Then the obtained crystal was dissolved into double distilled water again and recrystallized two times. Finally, the sample was placed in a vacuum desiccator at 310 K to dry in vacuum for 6 h, the final product was put into a weighing bottle and preserved in a desiccator.

Theoretical contents of C, H, N, Zn and Cl in the compound have been calculated to be 11.94, 5.01, 13.92, 16.26, and 52.87%, respectively. Chemical and elemental analysis (model: PE-2400, PerkinElmer, USA) have shown that practical contents of C, H, N, Zn, and Cl in the compound were 11.92, 4.98, 13.93, 16.29, and 52.88%, respectively. This shows that the mass fraction purity of the sample is higher than 0.995.

2.2. X-ray crystallography

A suitable single crystal (0.49 mm × 0.45 mm × 0.42 mm) of the complex was glued to the fine glass fiber and then mounted on Bruker Smart-1000 CCD diffractometer with Mo Kα radiation (λ = 0.071073 nm). The intensity data were collected in the φ–ω scan mode at T = 298(2) K. The empirical absorption corrections were based on multi-scan. The structure was solved by direct method and different Fourier syntheses, and all non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares method. All calculations were performed with the program package SHELXTL [5]. Crystal structure reports and structure-factor tables were summarized in Supporting Information.

2.3. Adiabatic calorimetry

A precision automatic adiabatic calorimeter was used to measure heat capacities of the compound over the temperature range $77 \leq (T/\mathrm{K}) \leq 377$. The calorimeter was established in the Thermochemistry Laboratory of the College of Chemistry and Chemical Engineering, Liaocheng University, China. The principle and performance of the adiabatic calorimeter and the procedures of heat capacity measurements have been described in detail elsewhere [6]. Heat-capacity measurements were continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The liquid nitrogen was used as a coolant. The heating rate and temperature increments were generally controlled at 0.1–0.4 K min^{-1} and 1–3 K. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were kept within 10^{-3}–10^{-4} K min^{-1} during the acquisition of all heat-capacity data. The data of heat capacities and corresponding equilibrium temperature have been corrected for heat exchange of the sample cell with its surroundings [6]. The reliability of the calorimeter had been confirmed by the measurement of the heat capacities of the reference standard material (α-Al_2O_3) over the temperature range $77 \leq (T/\mathrm{K}) \leq 400$. Deviations of the experimental results from those of the smoothed curve lie within ±0.20%, while the uncertainty is ±0.30%, as compared with the values given by the former National Bureau of Standards [7] over the whole temperature range.

The mass of the sample used in calorimetric measurements was 1.68015 g, which was equivalent to 0.00418 mol in terms of its molar mass, M = 402.31 g mol^{-1}.

2.4. Isoperibol solution-reaction calorimetry

The isoperibol solution-reaction calorimeter consists primarily of a precise temperature controlling system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precise temperature measuring system and a data acquisition system. The principle and structure of the calorimeter were described in detail elsewhere [8].

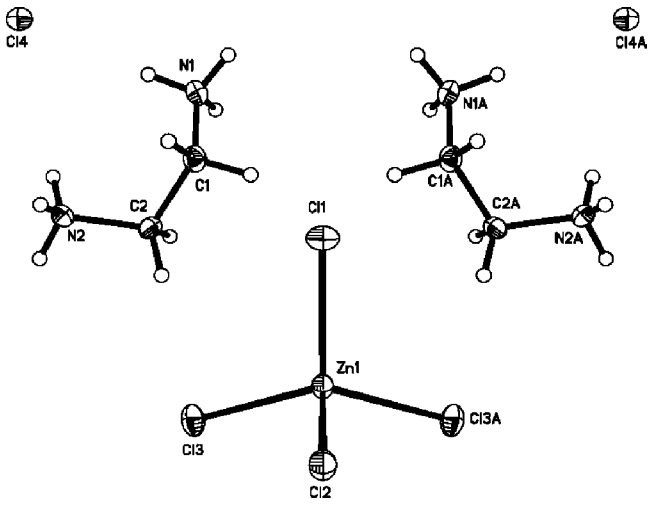

Fig. 1. Molecular structure of the title compound $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$(s).

The reliability of the calorimeter was verified previously by measuring dissolution enthalpy of KCl (calorimetric primary standard) in double distilled water at T = 298.15 K. According to the molar ratio of KCl to water, $n_{KCl} : n_{H_2O} \approx 1 : 1110$, KCl was dissolved in 100 cm^3 of double-distilled water at $T = (298.15 \pm 0.001)$ K. The mean dissolution enthalpy was (17,547 ± 13) J mol^{-1} for KCl, which compares with published data (17,536 ± 3.4) J mol^{-1} [9] under the same experimental condition. It shows that relative deviation between the literature value and the measuring value is within ±0.3%.

In all dissolution experiments of the sample, 100 cm^3 of double-distilled water was chosen as the calorimetric solvent for the measurement of the dissolution enthalpies.

3. Results and discussion

3.1. Crystal structure of $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$

The molecular structure of the title complex is shown in Fig. 1. The molecular unit of the complex consists of two protonated ethylenediamines, one tetrachlorozincate(II) anion, and two Cl^- anions. Crystal system of the complex is orthorhombic with space group *Pnma* and cell parameters a = 1.28746(12) nm, b = 1.91948(19) nm, c = 0.61729(8) nm, and $\alpha = \beta = \gamma = 90^\circ$, respectively, as shown in Supporting Information, in which the cell parameters are almost the same as those measured by Deeth et al. [10]. Just as described by Willian T.A. Harrison who published the article about the title ethylenediaminium tetrachlorozincate [11]: "$(C_2H_{10}N_2)_2[ZnCl_6]$ reported by Deeth et al. in 1984 is probably better formulated as $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$, it contains tetrachlorozincate anions as well as two 'free' Cl^- ions, and not $[ZnCl_6]^{4-}$ moieties".

In our present paper, the crystal parameters of the title complex are the same as the $(C_2H_{10}N_2)_2[ZnCl_6]$ reported by Deeth et al. in 1984, so it can be assured that the structural formula of the title compound should be $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$. The Zn atom is tetrahedrally bound by four chlorine atoms (the other two chlorine atoms are dissociative) to form a distorted tetrahedron, and not a hexacoordinated complex. The bond lengths of Zn(1)–Cl(1), Zn(1)–Cl(2), Zn(1)–Cl(3), and Zn(1)–Cl(3A) are 0.22765(9) nm, 0.23214(9) nm, 0.22498(6) nm, and 0.22497(6) nm, respectively, in which the later two Zn–Cl bond lengths are shorter than the other two and there is a maximum difference of

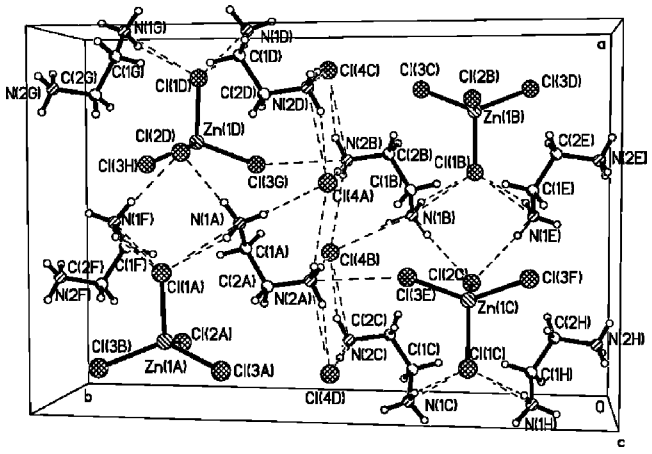

Fig. 2. Packing diagram of structure of the title compound binding together through hydrogen bonds.

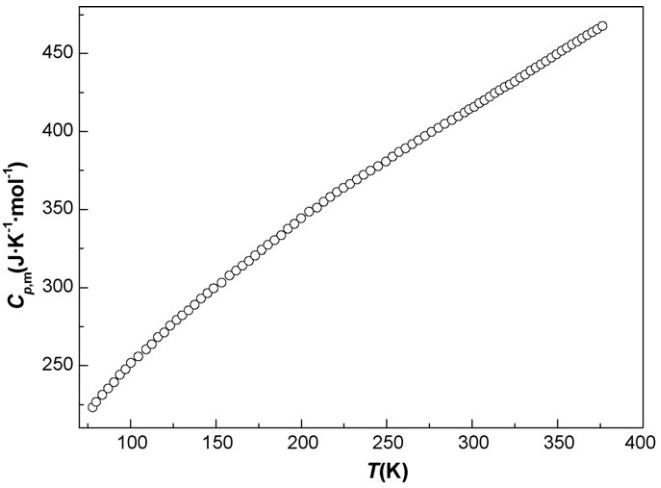

Fig. 3. Experimental molar heat capacities of the title compound.

0.00714 nm. It may be caused by the absence of hydrogen bonds between the atoms of Cl(3) and N. In addition, the bond angles (see Supporting Information) present the significant deviation from the compressed angle 103.69(2)° of Cl(3)–Zn(1)–Cl(2) to the extended angle 125.02(3)° of Cl(3A)–Zn(1)–Cl(3), and lead to a difference of 21.33°, which is similar to the structure of $[CoCl_4]^{2-}$ anion in $(C_2H_{10}N_2)_2(CoCl_4)Cl_2$ [12].

Two protons link directly with two nitrogen atoms in each ethylenediamine and divalent cation is formed. Imidogens in the ethylenediamine readily get protons in the acidic medium rather than coordinate with zinc atom even though the nitrogen atoms of the ethylenediamine have a strong coordination ability [13,14]. The $[ZnCl_4]^{2-}$ anions and Cl^- anions bind with the $[H_3NCH_2CH_2NH_3]^{2+}$ cations through electrostatic attraction as well as several hydrogen bonds (see Supporting Information). This symmetric unit is stacked antisymmetrically, and give rise to an infinite waved chain when viewing along the *c*-axis, and on account of binding action of hydrogen bonds, the molecule unit extend to a space supermolecule, which helps to establish a space crystal packing (see Fig. 2). The results indicate that the hydrogen bonds play an important role in the stabilization of the whole structure.

3.2. Low-temperature heat capacities

The experimental molar heat capacities of the complex were listed in Supporting Information and plotted in Fig. 3. It can be seen from Fig. 3 that the heat capacities smoothly and continuously increased with the temperature in the temperature region from 77 to 377 K, which showed that the structure of the complex was stable over the temperature range, no phase change, association, and thermal decomposition occurred. The polynomial equation of experimental molar heat capacities ($C_{p,m}$) vs. reduced temperature (X), $X = f(T)$, was fitted by least square method:

$$C_{p,m}(\mathrm{J\,K^{-1}mol^{-1}}) = 364.63173 + 111.45748X - 18.88566X^2 + 11.00815X^3 + 0.41447X^4 \quad (1)$$

in which $X = (T–227)/150$. The correlation coefficient for the fitting $R^2 = 0.99995$. In which 227 is half of the upper limit 377 K plus the lower limit 77 K, while 150 is half of the upper limit 377 K minus the lower limit 77 K. The reduced temperature (X) obtained using the method are placed between +1 and −1, and relative deviations of the smoothed heat capacities from the experimental values will become smaller and smaller with the increase of the power in the equation according to the statistical principle. The above equation is valid in the temperature range from $T = 77$ to $T = 377$ K, and the relative deviations, $RD/\% = [(C_{exp} - C_{smo})/C_{smo}] \times 100\%$, of the experimental molar heat capacities of the compound from the smoothed values against the absolute temperature is ±0.4% except for several points around the lower temperature limit, as shown in Fig. 4.

3.3. The smoothed heat capacities and thermodynamic functions of the complex

The smoothed molar heat capacities and thermodynamic functions of the sample were calculated based on the fitted polynomial equation of the heat capacity as a function of the reduced temperature (X) according to the following thermodynamic equations:

$$(H_T - H_{298.15}) = \int_{298.15}^{T} C_{p,m}\mathrm{d}T \quad (2)$$

$$(S_T - S_{298.15}) = \int_{298.15}^{T} C_{p,m} \cdot T^{-1}\mathrm{d}T \quad (3)$$

The smoothed heat capacities and thermodynamic functions of the compound relative to the standard reference temperature 298.15 K were tabulated in Table 1 at intervals of 5 K.

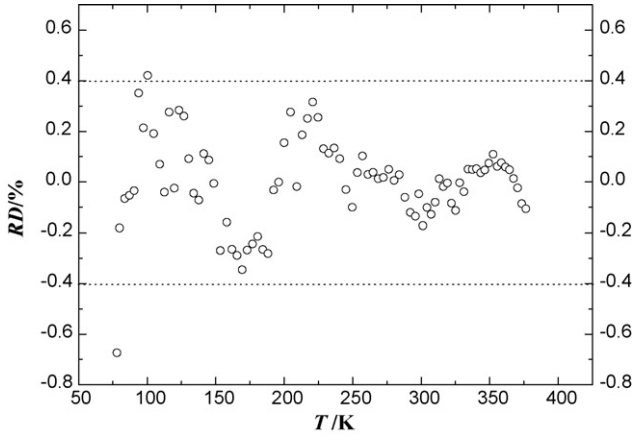

Fig. 4. The plot of the relative deviations, $RD/\% = [(C_{exp} - C_{smo})/C_{smo}] \times 100\%$, of the smoothed molar heat capacities of the compound from the experimental values against the absolute temperature. In which C_{smo} and C_{exp} represent the smoothed and experimental molar heat capacities of the compound, respectively.

Table 1
Smoothed heat capacities and thermodynamic functions of $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$(s).

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	$H_T - H_{298.15}$ (kJ mol^{-1})	$S_T - S_{298.15}$ (J K^{-1} mol^{-1})
80	227.287	−72.06	−408.1
85	233.188	−70.91	−394.2
90	238.981	−69.73	−380.7
95	244.671	−68.52	−367.6
100	250.258	−67.28	−354.9
105	255.745	−66.02	−342.5
110	261.134	−64.72	−330.5
115	266.428	−63.41	−318.7
120	271.627	−62.06	−307.3
125	276.735	−60.69	−296.1
130	281.754	−59.29	−285.1
135	286.686	−57.87	−274.4
140	291.532	−56.43	−263.9
145	296.296	−54.96	−253.6
150	300.980	−53.46	−243.5
155	305.585	−51.95	−233.6
160	310.115	−50.41	−223.8
165	314.571	−48.85	−214.2
170	318.955	−47.26	−204.8
175	323.271	−45.66	−195.5
180	327.520	−44.03	−186.3
185	331.704	−42.38	−177.3
190	335.826	−40.71	−168.4
195	339.889	−39.02	−159.6
200	343.894	−37.31	−151.0
205	347.844	−35.58	−142.4
210	351.741	−33.83	−134.0
215	355.589	−32.07	−125.6
220	359.388	−30.28	−117.4
225	363.142	−28.47	−109.3
230	366.853	−26.65	−101.2
235	370.524	−24.80	−93.29
240	374.157	−22.94	−85.44
245	377.754	−21.06	−77.68
250	381.318	−19.16	−70.00
255	384.851	−17.25	−62.41
260	388.357	−15.32	−54.89
265	391.836	−13.37	−47.46
270	395.293	−11.40	−40.10
275	398.729	−9.413	−32.82
280	402.148	−7.411	−25.61
285	405.551	−5.392	−18.47
290	408.941	−3.355	−11.39
295	412.321	−1.302	−4.384
298.15	414.446	0	0
300	415.694	0.7679	2.563
302	417.041	1.601	5.325
310	422.426	4.959	16.28
315	425.792	7.079	23.05
320	429.161	9.217	29.78
325	432.535	11.37	36.45
330	435.917	13.54	43.07
335	439.311	15.73	49.65
340	442.718	17.94	56.18
345	446.142	20.16	62.67
350	449.585	22.40	69.12
355	453.050	24.65	75.53
360	456.540	26.93	81.90
365	460.057	29.22	88.23
370	463.604	31.53	94.52
375	467.184	33.86	100.8

3.4. The enthalpy change of the solid phase reaction and standard molar enthalpy of formation of the title complex

The solid-state coordination reaction of $NH_3CH_2CH_2NH_3Cl_2$ (s) with $ZnCl_2$ (s) was designed according to the following equation:

$$2C_2H_{10}N_2Cl_2(s) + ZnCl_2(s) \rightarrow (C_2H_{10}N_2)_2(ZnCl_4)Cl_2(s) \quad (4)$$

The standard molar enthalpies of dissolution for the reactants and product of the reaction (4) in the selected solvent (100 cm^{-3} double–distilled water) were measured by an isoperibol solution-reaction calorimeter, respectively. The enthalpy changes of the reaction was calculated from the data of above standard molar enthalpies of dissolution.

Before measuring the standard molar enthalpies of dissolution, the solid reactants (ethylenediamine dihydrochloride and $ZnCl_2$) and the product $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$ were, respectively, ground within an agate mortar into fine powder and placed in a vacuum desiccator at T = 300 K to dry in vacuum for 2 h, respectively.

The reactants and product of the reaction (4) were accurately weighed based on 1×10^{-3} mol of $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$ as a norm according to the stoichiometric coefficients of the reaction (4).

About 0.266 g of ethylenediamine dihydrochloride was accurately weighed and dissolved in 100 cm^{-3} of double-distilled water. The five experimental results of the dissolution enthalpy ($\Delta_s H^\circ_{(C_2H_{10}N_2)_2(ZnCl_4)Cl_2}$) were listed in Table 2. The final solution obtained was named as solution A_1. If "s" represented 100 cm^3 of double-distilled water, the dissolution process could be expressed as

$$\{C_2H_{10}N_2Cl_2(s)\} + \text{“}s\text{”} = \text{Solution}A_1$$

About 0.136 g of zinc chloride was accurately weighed and dissolved in solution A_1. The experimental results of dissolution enthalpy ($\Delta_s H^\circ_{ZnCl_2}$) were shown in Table 2. The dissolution process could be expressed as

$$\{ZnCl_2(s)\} + \text{“Solution}A_1\text{”} = \text{Solution}A$$

About 0.402 g of $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$(s) was accurately weighed and dissolved in 100 cm^3 of double-distilled water. The dissolution process was expressed as

$$\{(C_2H_{10}N_2)_2(ZnCl_4)Cl_2(s)\} + \text{“s”} = \text{Solution}B$$

And the detailed results ($\Delta_s H^\circ_{(C_2H_{10}N_2)_2(ZnCl_4)Cl_2}$) obtained from five tests were listed in Table 2.

Then, the enthalpy change of the reaction (4) can be calculated from the data of above molar enthalpies of dissolution:

$$\begin{aligned}
\Delta_r H^\circ_m &= \sum \Delta_s H^\circ_m(\text{reactants}) - \sum \Delta_s H^\circ_m(\text{product}) \\
&= 2 \times \Delta_s H^\circ_{C_2H_{10}N_2} + \Delta_s H^\circ_{ZnCl_2} - \Delta_s H^\circ_{(C_2H_{10}N_2)_2(ZnCl_4)Cl_2} \\
&= 2 \times \Delta H_1 + \Delta H_2 - \Delta H_3 \\
&= 2 \times 20.4 + (-42.2) - 16.5 \\
&= -(17.9 \pm 0.6)\,\text{kJ mol}^{-1}.
\end{aligned}$$

A reaction scheme used to derive the standard molar enthalpies of formation of $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$ (s) were given in Table 3. The experimental values of the dissolution enthalpies of the reactants and product were combined with some auxiliary thermodynamic data, $\Delta_f H^\circ_m$ ($C_2H_{10}N_2Cl_2$, s) = −(540.74 ± 1.33) kJ mol^{-1} [15], and $\Delta_f H^\circ_m$ ($ZnCl_2$, s) = −415.05 kJ mol^{-1} [16]. The standard molar enthalpy of formation of $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$ was derived to be:

$$\begin{aligned}
&\Delta_f H^\circ_m[(C_2H_{10}N_2)_2(ZnCl_4)Cl_{2,s}] = \Delta_r H^\circ_m + 2 \\
&\quad \times \Delta_f H^\circ_m[C_2H_{10}N_2Cl_{2,s}] + \Delta_f H^\circ_m[ZnCl_{2,s}] \\
&= 2 \times \Delta H_1 + \Delta H_2 - \Delta H_3 + 2 \times \Delta H_4 + \Delta H_5 \\
&= -17.9 + 2 \times (-540.74) + (-415.05) \\
&= -(1514.4 \pm 2.7)\text{kJ mol}^{-1}.
\end{aligned}$$

The UV/Vis spectroscopy and refractive index are two important methods to determine whether the chemical composition and physicochemical properties of two solutions are same or not. The results of UV/Vis spectra were plotted in Fig. 5, which showed that UV–Vis spectra of solution A was almost identical with that of solution B, and refractive indexes were determined to be (1.3337 ± 0.0007) for the solution A and (1.3336 ± 0.0006) for solution B, which showed that the solutions A and B were in the same thermodynamic state. Therefore, the designed Hess

Table 2
Dissolution enthalpies of reactants and product of reaction (4) in the 100 cm^3 of double-distilled water (T = 298.15K).[a]

System	Solvent	No.	W (g)	$\Delta E_s/\Delta E_e$	t_e (s)	Q_s (J)	$\Delta_s H_m^\circ$ (kJ mol^{-1})
$C_2H_{10}N_2Cl_2$	Double-distilled water	1	0.26634	−1.1854	72.656	41.924	20.938
		2	0.26655	−1.1743	71.562	40.905	20.413
		3	0.26630	−1.1720	71.968	41.057	20.508
		4	0.26627	−1.1183	72.141	39.269	19.617
		5	0.26651	−1.1522	72.969	40.925	20.427
	$(\bar{x} \pm \sigma_a)$			$\Delta_s H^\circ_{C_2H_{10}N_2Cl_2} = (20.4 \pm 0.2)$ kJ mol^{-1}			
$ZnCl_2$	Solution A	1	0.13650	1.0812	81.672	−42.984	−42.921
		2	0.13604	1.0135	82.140	−41.721	−41.801
		3	0.13650	1.0293	82.875	−41.524	−41.463
		4	0.13692	1.0281	83.765	−41.918	−41.728
		5	0.13682	1.0612	83.438	−43.099	−42.935
	$(\bar{x} \pm \sigma_a)$			$\Delta_s H^\circ_{ZnCl_2} = -(42.2 \pm 0.3)$ kJ mol^{-1}			
$(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$	Double-distilled water	1	0.40250	−0.7689	45.421	17.000	16.994
		2	0.40218	−0.9148	36.547	16.276	16.283
		3	0.40248	−0.9264	34.438	15.528	15.523
		4	0.40232	−0.9854	34.954	16.766	16.767
		5	0.40205	−1.1519	29.983	16.813	16.825
	$(\bar{x} \pm \sigma_a)$			$\Delta_s H^\circ_{(C_2H_{10}N_2)_2(ZnCl_4)Cl_2} = (16.5 \pm 0.3)$ kJ mol^{-1}			

[a] In which: W is mass of sample; ΔE_s is the voltage change during the sample dissolution; ΔE_e is the voltage change during the electrical calibration; t_e is heating duration of electrical calibration; Q_s is heat effect of sample dissolution; $\Delta_s H_m^\circ$ is dissolution enthalpy, $\Delta_s H_m^\circ = Q_s/n = -(\Delta E_s/\Delta E_e) I^2 R t_e (M/W)$, where R is the electrical resistance of the heater in the reaction vessel (R = 1216.9 Ω at T = 298.15 K); I is the current through the heater (I = 20.015 mA) and M is the molar mass of the sample; $\bar{x}$ is the mean value of a set of measurement results; $\sigma_a = \sqrt{\sum_{i=1}^{n}(x-\bar{x})^2/n(n-1)}$, n is the experimental number; x_i is a single value in a set of measurements.

Table 3
Reaction scheme used to determine the standard molar enthalpy of formation of $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$(s).

No.	Reactions	Formed Solution	$\Delta_f H_m^o$ or $(\Delta_s H_m^o \pm \sigma_a)$ (kJ mol^{-1})
1	$\{C_2H_{10}N_2Cl_2(s)\}$ + "s"=	A	(20.4 ± 0.2), ΔH_1
2	$\{ZnCl_2(s)\}$ + solution A=	A_1	−(42.2 ± 0.3), ΔH_2
3	$\{(C_2H_{10}N_2)_2(ZnCl_4)Cl_2(s)\}$ + "s"=	B_1	(16.5 ± 0.3), ΔH_3
4	$2C(s) + 5H_2(g) + N_2(g) + Cl_2(g) = C_2H_{10}N_2Cl_2(s)$		−(540.74 ± 1.33), ΔH_4
5	$Zn(s) + Cl_2(g) = ZnCl_2(s)$		−415.05, ΔH_5
6	$4C(s) + 10H_2(g) + 2N_2(g) + 3Cl_2(g) + Zn(s) = (C_2H_{10}N_2)_2(ZnCl_4)Cl_2(s)$		−(1514.4 ± 2.7), ΔH_6

thermochemical cycle was reasonable and can be used to calculate standard molar enthalpy of formation of the title complex $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$(s).

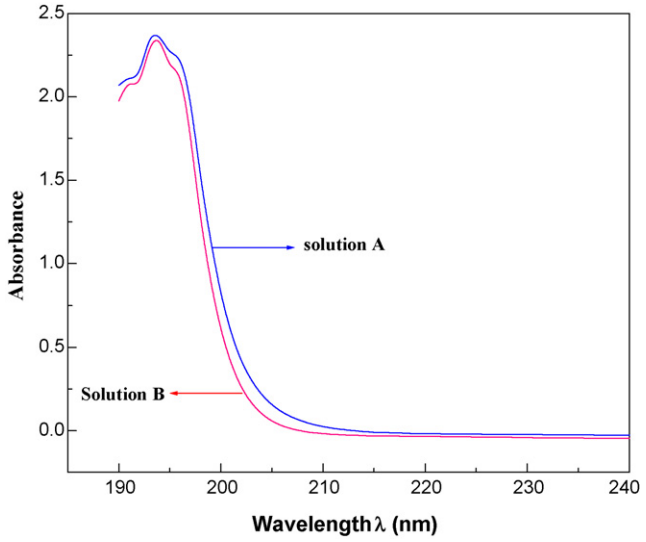

Fig. 5. UV–vis spectra of solution A_1 and solution B_1.

4. Conclusions

The crystal structure, low-temperature heat capacities, and standard molar enthalpy of formation of the title complex $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$(s) are reported in the paper. The enthalpy change of the designed thermochemical reaction is calculated to be $\Delta_r H_m^\circ = -(17.9 \pm 0.6)$ kJ mol^{-1}. The standard molar enthalpy of formation of the compound $(C_2H_{10}N_2)_2(ZnCl_4)Cl_2$ (s) is a negative value with large absolute value, which indicated that it has lower energy and more stable structure in comparison with the stable elementary substances which it is made up from.

Acknowledgement

This work was financially supported by the National Natural Science Foundations of China under the contract NSFC No. 20673050 and 20973089.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2010.04.012.

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