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Low-Temperature Heat Capacities and Standard Molar Enthalpy of Formation of Dichloro Bis(2-aminopyridine) Zinc (II), $ZnCl_2(C_5H_6N_2)_2(s)$

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Abstract Dichloro bis(2-aminopyridine) zinc (II), $ZnCl_2(C_5H_6N_2)_2(s)$, was synthesized by the method of solvonthermal synthesis in which 2-aminopyridine and zinc chloride were chosen as the reactants. X-ray crystallography, chemical analysis, and elemental analysis were applied to characterize the structure and composition of the complex. Low-temperature heat capacities of the title compound were measured with a precise small-sample automated adiabatic calorimeter over the temperature range from 78 K to 398 K. A polynomial equation of the heat capacities as a function of temperature was fitted by a least-squares method. Smoothed heat capacities and thermodynamic functions of the compound relative to the standard reference temperature (298.15 K) were calculated and tabulated at intervals of 5 K based on the fitted polynomial. A reasonable thermochemical cycle was designed, and the standard molar enthalpies of dissolution for the reactants and products of the synthesis reaction in a selected solvent were measured by an isoperibol solution-reaction calorimeter. In addition, the enthalpy change of the reaction was calculated from the data of the above standard molar enthalpies of dissolution. Finally, the standard molar enthalpy of formation of the complex $ZnCl_2(C_5H_6N_2)_2(s)$ was determined to be $-(400.52 \pm 1.66)\ kJ \cdot mol^{-1}$ in accordance with Hess's law.

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Keywords Dichloro bis(2-aminopyridine) zinc (II) · Low-temperature heat capacity · Standard molar enthalpy of dissolution · Standard molar enthalpy of formation · Thermodynamic function · X-ray crystallography

1 Introduction

2-Aminopyridine is an amino-containing heterocyclic compound and in a class of useful pyridine derivatives. It is used in large-scale industrial application. For example, a medicine, pesticide, and dye were prepared using 2-aminopyridine [1]. It is also a reagent often used for analytical chemistry and medical detection [2]. The complexes formed by the coordination of 2-aminopyridine with biological metal ions have good magnetic properties, biological activity, and structural diversity, which can serve as prodrugs such as anti-tumor, anti-bacterial, and anti-cancer agents [3]. In addition, some metal-pyridine coordination compounds have been explored for the design of a new nonlinear optical material [4]. It is well known that zinc is one of the trace elements necessary for good human and animal health. It is a component of many enzymes in the biological body. A shortage of zinc in the human body can result in many kinds of diseases including diabetes and hypertension. The title compound may be used as a compound medicine.

Qing et al. [4] synthesized the title compound and investigated its crystal structure. However, some important thermodynamic properties of the title compound, e.g., low-temperature heat capacities and standard molar enthalpies of formation, have not been found in the literature, which has restricted the progress of relevant theoretical studies and application development of the compounds. The heat capacity and standard molar enthalpy of formation of a substance are some of the most fundamental thermodynamic properties and closely related to other physical, biological, physiological, and chemical properties [5,6]. The standard molar enthalpy of formation of a substance is one of the important data required when calculating enthalpy changes, equilibrium constants, and theoretical yields of reactions in which the substance is involved. The purpose of this study is to measure low-temperature heat capacities of the compound by adiabatic calorimetry and the dissolution enthalpies of the reactants and product of a designed thermochemical reaction by isoperibol solution-reaction calorimetry; thermodynamic functions and the standard molar enthalpy of formation of the title compound were derived from these experimental results.

2 Experimental

2.1 Synthesis and Characterization of the Complex $ZnCl_2(C_5H_6N_2)_2$

Zinc chloride and 2-aminopyridine used as the reactants were of analytical grade with a labeled mass percent purity of 99.0 %. 2-Aminopyridine was further purified using light petroleum. The reactants were accurately weighed at the molar ratio of $n(ZnCl_2) : n(C_5H_6N_2) = 1 : 2$. A solution of 2-aminopyridine (2.900 g, 0.031 mol) in 35 cm^3 of ethanol and another solution of $ZnCl_2$ (2.100 g, 0.015 mol) in 30 cm^3 of ethanol were mixed together in a flask of 100 cm^3 volume. The solution was heated and stirred under reflux for 6 h. The final solution was naturally cooled to room temperature, filtered, and the crude product was washed three times with anhydrous ethanol. The white solid product was recrystallized using anhydrous ethanol, and colorless crystals were obtained. Finally, the sample was placed in a vacuum desiccator to dry in vacuum for 6 h at $T = 303\,\text{K}$. Theoretical mass percent contents of Zn, C, Cl, H, and N in the compound have been calculated to be (20.15, 37.01, 21.85, 3.73, and 17.26) %, respectively. Chemical and element analyses (Model PE-2400, Perkin Elmer, USA) have shown that the practical mass percent contents of Zn, C, H, and N in the compound have been measured to be (20.17, 36.9, 3.74, and 17.27) %, respectively. This showed the mass percent purity of the sample prepared was higher than 99.50 %. The content of zinc in the sample was measured by EDTA complex titration.

A single crystal with dimensions of 0.42 mm × 0.38 mm × 0.30 mm suitable for X-ray analysis was mounted on a fiber. All diffraction data for the compound were collected on a Bruker Smart-1000 CCD area-detector diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. The structure was solved by direct methods and expanded using Fourier techniques with the SHELXL-97 program [7] and refined with a full-matrix least-squares technique on F^2. All non-hydrogen atoms were refined anisotropically. All H-atoms were located theoretically and refined. Absorption corrections were applied by SADABS. Crystal data and refinement details are summarized in Table 1.

2.2 Adiabatic Calorimetry

A precise automatic adiabatic calorimeter was used to measure heat capacities of the compound over the temperature range $78 \leq (T/\text{K}) \leq 398$. The calorimeter was established in the Thermochemistry Laboratory of Liaocheng University, Shandong Province, China. The principle and structure of the adiabatic calorimeter have been described in detail elsewhere [8,9]. Briefly, the calorimeter comprised mainly a sample cell; a platinum resistance thermometer; an electric heater; inner, middle, and outer adiabatic shields; three sets of six-junction chromel-constantan thermopiles installed between the calorimetric cell and the inner shield, between the inner and middle shields, and between the middle and outer shields; and a high vacuum can. The miniature platinum resistance thermometer (IPRT No. 2, produced by the Shanghai Institute of Industrial Automatic Meters, 16 mm in length, 1.6 mm in diameter, and a nominal resistance of 100 Ω) was used to measure the temperature of the sample. The thermometer was calibrated on the basis of ITS-90 by the Station of Low-Temperature Metrology and Measurements, Academia Sinica. The electrical energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded by use of a data acquisition/switch unit (Model 34970A, Agilent, USA), and processed on-line by a computer.

To verify the performance of the calorimeter, the heat capacities of the reference standard material (α-Al_2O_3) were measured over the temperature range $78 \leq (T/\text{K}) \leq 400$. The sample mass used was 1.7143 g, which was equivalent to 0.0168 mol based on its molar mass, $M(Al_2O_3) = 101.9613\ \text{g} \cdot \text{mol}^{-1}$. The experimental molar heat capacities of α-Al_2O_3 were fitted by a least-squares method to a

Table 1 Crystal data and structure refinement for $ZnCl_2(C_5H_6N_2)_2(s)$

Crystallographic data	Structure refinement
Empirical formula	$C_{10}H_{12}Cl_2N_4Zn$
Formula weight	324.51
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pba2
Unit cell dimensions	$a = 7.7477(7)$ Å, $b = 12.0736(13)$ Å, $c = 6.8990(5)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$
Volume	645.35(10) Å^3
Z	2
Calculated density	$1.670\ g \cdot cm^{-3}$
Absorption coefficient	$2.299\ mm^{-1}$
F(000)	328
Crystal size	0.42 mm × 0.38 mm × 0.30 mm
θ range for data collection	2.95° to 25.01°
Limiting indices	$-8 \leq h \leq 9, -13 \leq k \leq 14, -8 \leq l \leq 7$
Reflections collected/unique	3000/1096 [R(int) = 0.0431]
Completeness to $\theta = 24.99$	99.4 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1096/1/78
Goodness-of-fit on F^2	1.042
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0270, wR_2 = 0.0581$
R indices (all data)	$R_1 = 0.0439, wR_2 = 0.0669$
Absolute structure parameter	0.01(2)
Largest diff. peak and hole	258 and $-316\ e \cdot nm^{-3}$

polynomial equation. Relative deviations of the experimental results from those of the smoothed curve lie within ±0.29 %, while the uncertainty is 0.30 %, as compared with the values given by the former National Bureau of Standards [10] over the whole temperature range.

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 heating rate and temperature increments were generally controlled at (0.1 to 0.4) $K \cdot min^{-1}$ and (1 to 3) K. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within (10^{-3} to 10^{-4}) $K \cdot min^{-1}$ during the acquisition of all heat-capacity data. The data of heat capacities and corresponding equilibrium temperatures have been corrected for heat exchange of the sample cell with its surroundings [8].

2.3 Isoperibol Solution-Reaction Calorimetry

The isoperibol solution-reaction calorimeter consisted 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 have been described in detail elsewhere [11].

The thermistor was adopted as the sensor for controlling temperature in the thermostatic bath. But the input signal of the modified high-precision temperature controller (Model DWT-702, manufactured by Shanghai No. 6 Automated Instrumentation Works), which operated in the proportional-integral-derivative (PID) mode, was not fed directly from the thermistor sensor, but from the signal of the self-made Wheatstone electric bridge used for temperature control. The water was used as the thermostatic medium. During the whole experiment, the water thermostat was automatically maintained at $T = (298.150 \pm 0.001)$ K by regulating an adjustable precise resistor in the Wheatstone bridge. Experiments have demonstrated that the precision of the temperature control of this kind of system can reach $\pm 1 \times 10^{-3}$ K.

The calorimetric body consisted of the calorimetric chamber, the electric stirrer, the temperature measurement system, and the sampling system. The measuring temperature system consisted of a similar Wheatstone electric bridge to that of the temperature control system and another thermistor with a large negative temperature coefficient of resistance. The thermistor used as a thermometer was calibrated on the basis of ITS-90 by the station of Low-temperature Metrology and Measurements, Academia Sinica. A data acquisition/switch unit (Model 34970A, Agilent, USA) was used to determine the temperature of the solution in the chamber with an uncertainty of 0.1 mK. The unbalanced voltage signal was a linear response to the change of temperature over the temperature range from (295 to 310) K. Measurements indicated that the precision of the temperature measurement system can reach $\pm 1 \times 10^{-4}$ K, and the time constant of the calorimeter was about 3 s. The system of electric energy calibration consisted of the electric heater and the precision power supply with stepwise constant currents. During each electrical energy calibration, the electrical current through the heater was set at $I = 20.015$ mA, and the resistance of the electrical heater was $R = 1213.09\ \Omega$ at $T = 298.15$ K.

The reliability of the calorimeter was verified previously by measuring the dissolution enthalpy of KCl (calorimetrical primary standard) in double distilled water. According to the molar ratio of KCl to H_2O, $n_{\mathrm{KCl}} : n_{\mathrm{H_2O}} \approx 1 : 1110$, the KCl was dissolved in $100\ \mathrm{cm}^3$ of double-distilled water at $T = (298.15 \pm 0.001)$ K. The mean dissolution enthalpy was $(17547 \pm 13)\ \mathrm{J \cdot mol^{-1}}$ for KCl, which compares with corresponding published data, $(17536 \pm 3.4)\ \mathrm{J \cdot mol^{-1}}$ [12].

In all dissolution experiments of the sample, $100\ \mathrm{cm}^3$ of $2.0\ \mathrm{mol \cdot dm^{-3}}$ HCl was chosen as the calorimetric solvent for measuring the dissolution enthalpies of the reactants and products at $T = 298.15$ K.

Finally, UV/vis spectra and the data of the refractive indexes were used to confirm whether the initial solution was in the same thermodynamic state as that of the reacted solution.

3 Results and Discussion

3.1 Crystal Structure

The molecular structure of $ZnCl_2(C_5H_6N_2)_2(s)$ is shown in Fig. 1. The selected bond lengths and angles of the title compound are listed in Table 2. Hydrogen bonds are listed in Table 3. Unit cell parameters are $a = 7.7477(7)$ Å, $b = 12.0736(13)$ Å, $c = 6.8990(5)$ Å, and $\alpha = \beta = \gamma = 90°$. It was found that the crystal system of the coordination compound is orthorhombic and the space group is *Pba*2, as shown in Table 1. A zinc atom is coordinated with two chlorine atoms and two nitrogen atoms on two pyridine rings. These atoms are arranged in a distorted tetrahedral configuration. The packing of the complex is shown in Fig. 2. It can be found from Fig. 2 that the intramolecular hydrogen bond and intermolecular hydrogen bond occurred in the crystal structure of the title compound and kept the crystal stable. The crystal data and the structure of the title compound determined were mostly consistent with the previously reported results [4].

3.2 Low-Temperature Heat Capacities

The experimental molar heat capacities of the coordination compound are listed in Table 4 and plotted in Fig. 3, which showed that the heat capacities of the compound increased smoothly with temperature. The title compound was thermally stable over the temperature range between $T = 78$ K and 398 K; no phase change, association, and thermal decomposition occurred. The experimental points in the temperature region between $T = 78$ K and $T = 398$ K were fitted by the least-squares method, and a polynomial equation of the experimental molar heat capacities ($C_{p,\mathrm{m}}$) versus reduced temperature (X), $X = f(T)$, has been obtained as follows:

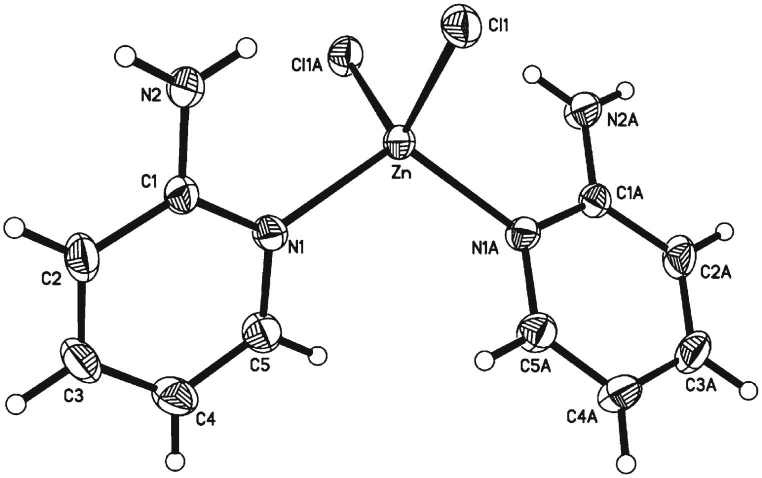

Fig. 1 Structure of the title compound $ZnCl_2(C_5H_6N_2)_2(s)$

Table 2 Selected bond lengths (Å) and angles (°) for $ZnCl_2(C_5H_6N_2)_2(s)$

Types of bonds	Bond length (Å)	Types of bond angles	Bond angle (°)
Zn–N(1)	2.039(3)	N(1)–Zn–N(1)#1	111.26(18)
Zn–N(1)#1	2.039(3)	N(1)–Zn–Cl(1)#1	105.37(8)
Zn–Cl(1)#1	2.2623(10)	N(1)#1–Zn–Cl(1)#1	111.45(8)
Zn–Cl(1)	2.2623(10)	N(1)–Zn–Cl(1)	111.45(8)
N(1)–C(1)	1.341(6)	N(1)#1–Zn–Cl(1)	105.37(8)
N(1)–C(5)	1.369(5)	Cl(1)#1–Zn–Cl(1)	112.08(6)
N(2)–C(1)	1.353(5)	C(1)–N(1)–C(5)	117.0(3)
N(2)–H(2A)	0.8600	C(1)–N(1)–Zn	123.2(3)
N(2)–H(2B)	0.8600	C(5)–N(1)–Zn	119.4(3)
C(1)–C(2)	1.394(7)	C(1)–N(2)–H(2A)	120.0
C(2)–C(3)	1.363(7)	N(1)–C(1)–N(2)	118.2(5)
C(2)–H(2)	0.9300	N(1)–C(1)–C(2)	122.2(4)
C(3)–C(4)	1.389(6)	N(2)–C(1)–C(2)	119.6(5)
C(3)–H(3)	0.9300	C(3)–C(2)–C(1)	119.3(4)
C(4)–C(5)	1.347(5)	C(3)–C(2)–H(2)	120.4
C(4)–H(4)	0.9300	C(4)–C(5)–N(1)	123.4(4)
C(5)–H(5)	0.9300	N(1)–C(5)–H(5)	118.3

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, z$

Table 3 Hydrogen bonds for $ZnCl_2(C_5H_6N_2)_2(s)$

D–H···A	d(D–H) (Å)	d(H···A) (Å)	∠DHA (°)	d(D···A) (Å)	Symmetry code of acceptor atom
N(2)–H(1A)···Cl(1)	0.86	2.53	149.5	3.304(4)	/
N(2)–H(1B)···Cl(1)	0.86	2.63	161.2	3.450(4)	$-x + 1/2, y + 1/2, z$

$$C_{p,\mathrm{m}}/(\mathrm{J\cdot mol^{-1}\cdot K^{-1}}) = 374.166 + 163.802\mathrm{X} - 29.990X^2 + 6.913X^3 + 8.075X^4 \tag{1}$$

in which $X = (T/\mathrm{K}-238)/160$. The correlation coefficient for the fitting (R^2) equaled 0.99999. The value, 238, is half of the upper limit 398 K plus half of the lower limit 78 K in the temperature range of (78 to 398) K, while 160 is half of the upper limit 398 K minus half of the lower limit 78 K in the same range. The reduced temperatures (X) obtained using this method are between +1 and −1, and relative deviations of the smoothed heat capacities from the experimental values will become smaller and smaller with an increase of the power of X in the fitted polynomial equation according to statistics.

Equation 1 is valid in the temperature range of (78 to 398) K. The relative deviations of the smoothed heat capacities obtained by the above equation from experimental heat capacities were within ±0.30 %, as shown in Fig. 4.

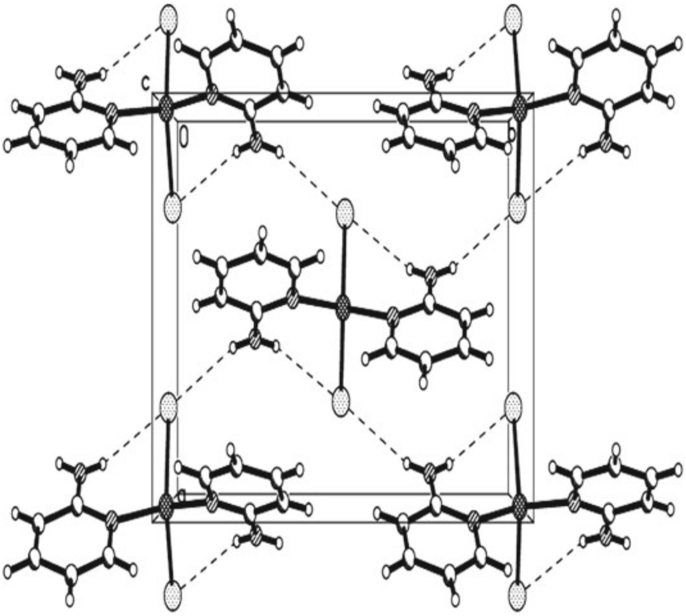

Fig. 2 Packing of structure of the title compound $ZnCl_2(C_5H_6N_2)_2(s)$ in unit cell

Table 4 Experimental molar heat capacities of $ZnCl_2(C_5H_6N_2)_2(s)$

T(K)	$C_{p,m}$ ($J \cdot mol^{-1} \cdot K^{-1}$)	T (K)	$C_{p,m}$ ($J \cdot mol^{-1} \cdot K^{-1}$)	T (K)	$C_{p,m}$ ($J \cdot mol^{-1} \cdot K^{-1}$)
78.4298	182.315	191.862	324.654	281.040	416.219
81.6833	186.528	194.080	327.460	283.332	418.155
84.9369	190.634	196.594	330.438	285.402	420.015
88.5602	195.539	198.960	332.920	287.695	422.558
91.8878	199.708	201.253	335.255	289.691	424.418
95.2153	203.705	203.323	337.796	291.762	426.771
98.3950	208.674	205.542	340.219	293.906	428.517
101.575	212.888	207.612	342.409	295.977	430.870
104.237	216.128	209.756	344.406	298.491	432.844
106.677	219.369	211.901	346.683	301.744	435.615
109.117	222.718	213.971	348.961	304.702	438.537
111.557	225.851	216.116	350.745	307.734	440.891
114.441	229.740	218.186	352.984	310.766	443.509
117.621	233.521	220.331	355.451	313.797	446.166
120.431	236.978	222.327	357.197	316.829	448.940
123.462	240.651	224.398	359.726	319.861	451.848
126.198	244.864	226.394	362.207	322.893	454.476
129.082	248.429	228.391	364.561	325.924	456.893
133.667	251.994	230.461	366.686	328.956	459.521

Table 4 continued

T(K)	$C_{p,\mathrm{m}}$ (J · mol^{-1} · K^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J · mol^{-1} · K^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J · mol^{-1} · K^{-1})
134.850	256.207	232.458	368.698	331.914	462.149
137.438	259.340	234.750	371.165	335.020	464.742
139.952	262.473	236.672	373.025	337.977	467.264
142.392	264.648	238.669	375.036	340.935	469.962
145.128	268.149	240.739	377.048	343.893	472.450
147.569	271.401	242.588	378.946	346.851	475.112
150.009	274.526	244.732	380.920	349.809	477.670
152.227	277.416	246.951	382.780	352.914	481.104
154.815	280.219	248.947	384.753	355.946	484.362
157.699	283.781	251.092	386.955	358.978	486.639
160.435	287.285	253.014	388.928	361.936	489.407
163.023	290.905	255.011	391.016	364.967	491.580
165.537	293.942	257.081	392.762	367.999	494.768
168.125	296.657	259.226	395.153	371.000	497.830
170.270	299.051	261.518	397.469	373.989	500.584
172.636	301.737	263.589	399.291	376.946	503.177
174.928	304.015	265.733	401.378	379.904	505.699
177.368	306.964	267.877	403.693	382.886	508.607
179.883	309.883	269.948	405.667	385.820	511.375
181.953	312.599	272.240	407.869	388.778	514.073
184.911	316.307	274.532	410.222	391.736	516.911
187.499	319.022	276.751	412.309	394.767	519.609
189.717	322.149	278.895	414.018	397.725	522.342

3.3 Thermodynamic Functions of the Compound

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

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

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

$$G_{(T)} - G_{(298.15\ \mathrm{K})} = \int_{298.15\ \mathrm{K}}^{T} C_{p,\mathrm{m}}\, \mathrm{d}T - T \int_{298.15\mathrm{K}}^{T} C_{p,\mathrm{m}} T^{-1}\, \mathrm{d}T \tag{4}$$

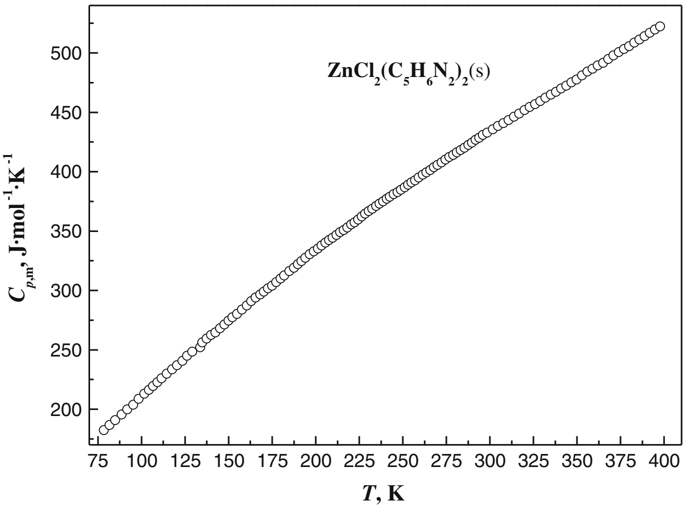

Fig. 3 Experimental molar heat capacities of $ZnCl_2(C_5H_6N_2)_2(s)$

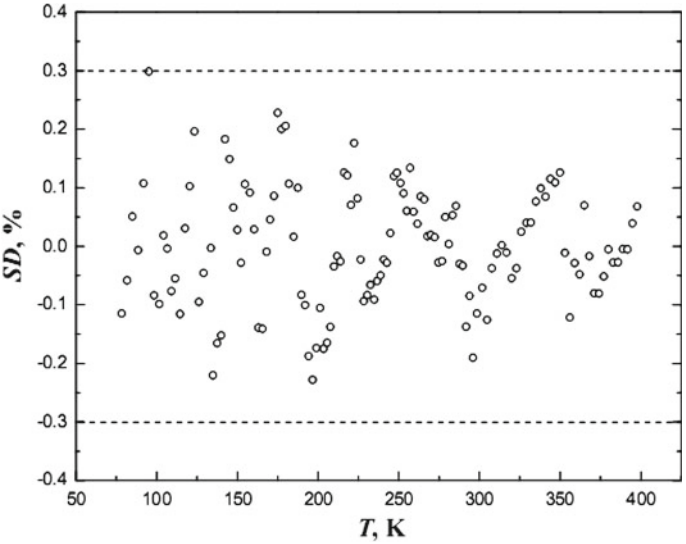

Fig. 4 Plot of the standard deviation of heat capacity of $ZnCl_2(C_5H_6N_2)_2(s)$ against the absolute temperature, $\mathrm{SD}/\% = [(C_{\mathrm{smo}} - C_{\mathrm{exp}})/C_{\mathrm{exp}}] \times 100\ \%$, C_{smo} and C_{exp} represent the smoothed and experimental molar heat capacities of the compound, respectively

The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of the sample relative to the standard reference temperature 298.15 K are tabulated in Table 5 at intervals of 5 K.

Table 5 Smoothed heat capacities and thermodynamic functions of $ZnCl_2(C_5H_6N_2)_2(s)$

T (K)	$C_{p,\mathrm{m}}$ $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	$H_T - H_{298.15\mathrm{K}}$ $(\mathrm{kJ \cdot mol^{-1}})$	$S_T - S_{298.15\mathrm{K}}$ $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	$G_T - G_{298.15\mathrm{K}}$ $(\mathrm{kJ \cdot mol^{-1}})$
80	184.19	−69.061	−381.03	−38.579
85	190.81	−68.124	−369.68	−36.701
90	197.43	−67.153	−358.58	−34.880
95	204.03	−66.149	−347.72	−33.116
100	210.61	−65.112	−337.07	−31.406
105	217.17	−64.043	−326.61	−29.749
110	223.70	−62.941	−316.34	−28.143
115	230.20	−61.806	−306.24	−26.588
120	236.67	−60.638	−296.30	−25.082
125	243.10	−59.439	−286.51	−23.626
130	249.49	−58.207	−276.85	−22.217
135	255.83	−56.944	−267.32	−20.856
140	262.13	−55.649	−257.91	−19.542
145	268.39	−54.323	−248.61	−18.274
150	274.59	−52.965	−239.42	−17.052
155	280.74	−51.577	−230.33	−15.876
160	286.84	−50.158	−221.33	−14.745
165	292.88	−48.708	−212.42	−13.658
170	298.87	−47.229	−203.60	−12.617
175	304.79	−45.720	−194.86	−11.619
180	310.66	−44.181	−186.20	−10.665
185	316.46	−42.613	−177.61	−9.7553
190	322.21	−41.017	−169.10	−8.8883
195	327.89	−39.391	−160.65	−8.0641
200	333.50	−37.738	−152.28	−7.2824
205	339.06	−36.056	−143.97	−6.5428
210	344.55	−34.347	−135.73	−5.8449
215	349.98	−32.611	−127.55	−5.1884
220	355.35	−30.848	−119.43	−4.5729
225	360.66	−29.057	−111.38	−3.9979
230	365.90	−27.241	−103.38	−3.4632
235	371.08	−25.399	−95.448	−2.9683
240	376.21	−23.530	−87.573	−2.5128
245	381.28	−21.637	−79.756	−2.0964
250	386.29	−19.718	−71.996	−1.7187
255	391.24	−17.774	−64.292	−1.3794
260	396.14	−15.805	−56.643	−1.0780
265	400.99	−13.812	−49.049	−0.81438
270	405.80	−11.795	−41.509	−0.58811
275	410.55	−9.7546	−34.020	−0.39895

Table 5 continued

T (K)	$C_{p,\mathrm{m}}$ $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	$H_T - H_{298.15\mathrm{K}}$ $(\mathrm{kJ \cdot mol^{-1}})$	$S_T - S_{298.15\mathrm{K}}$ $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	$G_T - G_{298.15\mathrm{K}}$ $(\mathrm{kJ \cdot mol^{-1}})$
280	415.26	−7.6900	−26.583	−0.24663
285	419.93	−5.6020	−19.197	−0.13094
290	424.56	−3.4907	−11.859	−0.051653
295	429.16	−1.3564	−4.5688	−0.0085967
298.15	432.04	0	0	0
300	433.72	0.80083	2.6748	−0.0016122
302	435.54	1.6701	5.5596	−0.0088879
310	442.77	5.1834	17.028	−0.095346
315	447.25	7.4085	24.141	−0.19586
320	451.73	9.6560	31.213	−0.33202
325	456.18	11.926	38.245	−0.50376
330	460.63	14.218	45.239	−0.71101
335	465.08	16.532	52.197	−0.95370
340	469.53	18.869	59.119	−1.2317
345	473.98	21.228	66.008	−1.5450
350	478.44	23.609	72.863	−1.8934
355	482.92	26.012	79.687	−2.2767
360	487.42	28.438	86.480	−2.6946
365	491.95	30.887	93.243	−3.1469
370	496.51	33.358	99.976	−3.6331
375	501.12	35.852	106.68	−4.1526
380	505.76	38.369	113.35	−4.7048
385	510.46	40.910	120.00	−5.2889
390	515.22	43.474	126.61	−5.9037
395	520.04	46.063	133.19	−6.5482

3.4 Standard Molar Enthalpy of Formation of the Complex

The designed reaction was shown as follows:

$$2\ \mathrm{C_5H_6N_2\ (s) + ZnCl_2\ (s) = ZnCl_2\ (C_5H_6N_2)_2\ (s)} \tag{5}$$

The enthalpy change of Eq. 5 can be determined by, respectively, measuring the enthalpies of dissolution of $\mathrm{ZnCl_2(s)}$ in 2.0 $\mathrm{mol \cdot dm^{-3}}$ of HCl solution, and $\mathrm{C_5H_6N_2(s)}$ in 2.0 $\mathrm{mol \cdot dm^{-3}}$ of HCl solution containing a certain amount of $\mathrm{ZnCl_2(s)}$ at 298.15 K.

First, 2-aminopyridine and zinc chloride must be dried in a vacuum desiccator at $T = 323\,\mathrm{K}$ for 4 h. About 6×10^{-4} mol or 0.0818 g of $\mathrm{ZnCl_2(s)}$ were dissolved in 100 $\mathrm{cm^3}$ of 2.0 $\mathrm{mol \cdot dm^{-3}}$ HCl at 298.15 K. If “S” denoted calorimetric solvent, 2.0 $\mathrm{mol \cdot dm^{-3}}$ of HCl, then,

$$\{\mathrm{ZnCl_2(s)}\} + \text{“S”} = \text{solution } \mathrm{A_1}.$$

According to $n(\mathrm{C_5H_6N_2}) : n(\mathrm{ZnCl_2}) = 2 : 1$ in Eq. 5, about 1.2×10^{-3} mol or 0.113 g of $\{\mathrm{C_5H_6N_2(s)}\}$ were dissolved in solution $\mathrm{A_1}$, namely,

$$\{\mathrm{C_5H_6N_2(s)}\} + \text{solution}\mathrm{A_1} = \text{solution A}.$$

About 6×10^{-4} mol or 0.195 g of $\{\mathrm{ZnCl_2(C_5H_6N_2)_2(s)}\}$ were dissolved in 100 $\mathrm{cm^3}$ of 2.0 $\mathrm{mol \cdot dm^{-3}}$ hydrochloride acid. The dissolution enthalpy of $\mathrm{ZnCl_2(C_5H_6N_2)_2}$ (s) in 2.0 $\mathrm{mol \cdot dm^{-3}}$ of HCl was measured under the same condition as the above,

$$\{\mathrm{ZnCl_2(C_5H_6N_2)_2(s)}\} + \text{“S”} = \text{solution B}.$$

The measurement results of dissolution enthalpies for the reactants and product of Eq. 5 are listed in Table 6.

The enthalpy change of Eq. 5 can be calculated in accordance with a thermochemical cycle and the experimental results of the dissolution enthalpy as follows,

$$\begin{aligned}\Delta_\mathrm{r} H^\circ_\mathrm{m}(5) &= \sum \Delta_\mathrm{s} H^\circ_\mathrm{m(Reactants)} - \sum \Delta_\mathrm{s} H^\circ_\mathrm{m(Products)}\\ &= \Delta_\mathrm{s} H^\circ_\mathrm{m,ZnCl_2} + 2\Delta_\mathrm{s} H^\circ_\mathrm{m,C_5H_6N_2} - \Delta_\mathrm{s} H^\circ_\mathrm{m,ZnCl_2(C_5H_6N_2)_2}\\ &= \Delta H_1 + 2\Delta H_2 - \Delta H_3\\ &= (-25.836) + 2(-21.566) - (-4.693)\\ &= -(64.275 \pm 0.461)\ \mathrm{kJ \cdot mol^{-1}}.\end{aligned}$$

The reaction scheme used to determine the standard molar enthalpy of formation of $\mathrm{ZnCl_2(C_5H_6N_2)_2(s)}$ is given in Table 6. The experimental values of the dissolution enthalpies of the reactants and product in Eq. 5 were combined with other auxiliary thermodynamic data of $\Delta_\mathrm{f} H^\circ_\mathrm{m}(\mathrm{ZnCl_2, s}) = -415.05\ \mathrm{kJ \cdot mol^{-1}}$ [13], and $\Delta_\mathrm{f} H^\circ_\mathrm{m}(\mathrm{C_5H_6N_{2,}s}) = (39.4 \pm 0.8)\ \mathrm{kJ \cdot mol^{-1}}$ [14], to derive the standard molar enthalpy of formation of $\mathrm{ZnCl_2(C_5H_6N_2)_2(s)}$,

$$\begin{aligned}&\Delta_\mathrm{f} H^\circ_\mathrm{m}\left[\mathrm{ZnCl_2\,(C_5H_6N_2)_2\,, s}\right] = \Delta H_6\\ &\quad = \Delta_\mathrm{r} H^\circ_\mathrm{m}(5) + \Delta_\mathrm{f} H^\circ_\mathrm{m}(\mathrm{ZnCl_2, s}) + 2\Delta_\mathrm{f} H^\circ_\mathrm{m}(\mathrm{C_5H_6N_2, s})\\ &\quad = \Delta_\mathrm{r} H^\circ_\mathrm{m} + 2\Delta H_4 + \Delta H_5 = \Delta H_1 + 2\Delta H_2 - \Delta H_3 + 2\Delta H_4 + \Delta H_5\\ &\quad = (-64.275) + 2 \times 39.4 + (-415.05) = -(400.52 \pm 1.66)\ \mathrm{kJ \cdot mol^{-1}},\end{aligned}$$

in which ΔH_1 to ΔH_6 were the standard molar enthalpies of dissolution of reactants and product, and the standard molar enthalpies of formation of reactants and product corresponding to the number of reactions in Table 6.

In this article, all the reactants and product in Eq. 5 can be easily dissolved in the corresponding solvents. The results of UV/vis spectra of solution A obtained from dissolution of the reactants and solution B from dissolution of the products are shown in Fig. 5. The experimental values of the refractive indexes of solutions A and B were measured to be (1.3491 ± 0.0004) and (1.3489 ± 0.0003), respectively. These results indicated that solution A was consistent with solution B. Therefore, there was no difference in the structure, chemical components, and physicochemical properties

Table 6 Dissolution enthalpies of reactants and products of Eq. 5 in the selected solvents at $T = 298.15$ K

System	Solvent	Avg.$\Delta_s H_m^\circ$ (kJ · mol^{-1})	No.	m(g)	$\Delta E_s/\Delta E_e$	t_e (s)	Q_s (J)	$\Delta_s H_m^\circ$ (kJ · mol^{-1})
Zinc chloride	2.0 mol · dm^{-3}HCl	−(25.836 ± 0.163)	1	0.0820	1.0783	29.578	−15.499	−25.765
			2	0.0813	1.0769	29.015	−15.184	−25.460
			3	0.0809	1.1496	28.093	−15.695	−26.445
			4	0.0820	1.0827	29.578	−15.499	−25.765
			5	0.0816	1.1759	26.969	−15.412	−25.745
2-Aminopyridine	Solution A_1	−(21.566 ± 0.211)	1	0.1133	1.9486	26.719	−25.302	−21.016
			2	0.1123	1.5715	33.922	−25.906	−21.710
			3	0.1127	1.2966	42.312	−26.662	−22.264
			4	0.1124	1.1123	47.031	−25.423	−21.286
			5	0.1126	1.0560	50.250	−25.788	−21.554
Dichloro bis(2-aminopyridine) zinc (II)	2.0 mol · dm^{-3}HCl	−(4.693 ± 0.088)	1	0.1938	0.3015	20.031	−2.9352	−4.9153
			2	0.1938	0.5316	11.219	−2.8981	−4.8532
			3	0.1942	0.5744	9.656	−2.6956	−4.5048
			4	0.1941	0.5758	10.062	−2.8157	−4.7079
			5	0.1939	0.6379	8.640	−2.6782	−4.4827

m (g) mass of sample, t_e (s) heating period of electrical calibration, $Q_s = -(\Delta E_s/\Delta E_e) \cdot I^2 R t_e$ heat effect during the sample dissolution, ΔE_s (mV) the voltage change during the sample dissolution, ΔE_e (mV) the voltage change during the electrical calibration, $\Delta_s H_m^\circ = Q_s/n = -(\Delta E_s/\Delta E_e) \cdot I^2 R t_e (M/m)$ where R is the electro-resistance ($R = 1213.09\ \Omega$ at $T = 298.15$ K), I is the current ($I = 20.015$ mA), and M is the molar mass of the sample

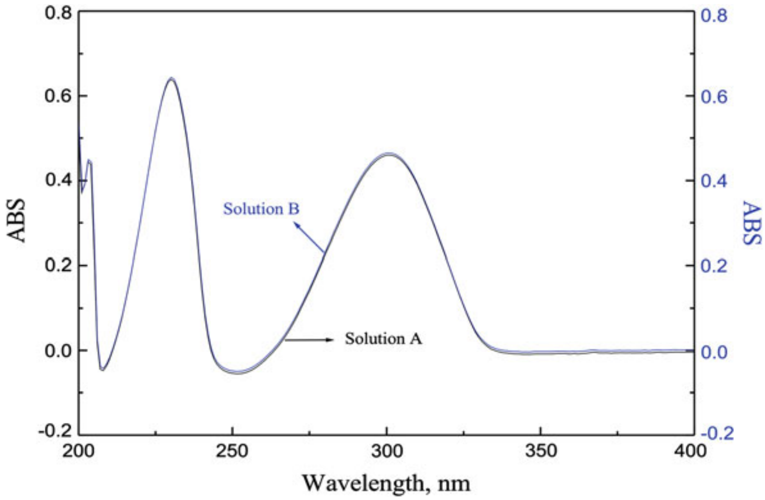

Fig. 5 UV/vis spectra of solution A obtained from dissolution of the reactants and solution B from dissolution of the product (diluted to 1:20)

Table 7 Reaction scheme used to determine the standard molar enthalpy of formation of $ZnCl_2(C_5H_6N_2)_2(s)$

No.	Reactions	Formed solution	$\Delta_f H_m^\circ$ or $(\Delta_s H_m^\circ \pm \sigma_a)^a$ $(kJ \cdot mol^{-1})$
1	$\{ZnCl_2 (s)(s)\}$ + "S"=	A_1	$-(25.836 \pm 0.163)$, ΔH_1
2	$\{C_5H_6N_2 (s)\}$ + solution A_1=	A	$-(21.566 \pm 0.211)$, ΔH_2
3	$\{ZnCl_2(C_5H_6N_2)_2(s)\}$ + "S"=	B	$-(4.693 \pm 0.088)$, ΔH_3
4	$5C(s) + 3 H_2(g) + N_2(g) = C_5H_5N_2(s)$		(39.4 ± 0.8), ΔH_4
5	$Zn(s) + Cl_2(g) = ZnCl_2 (s)$		-415.05, ΔH_5
6	$Zn(s)+Cl_2(g)+10C(s)+6H_2(g) +2N_2(g)=ZnCl_2(C_5H_6N_2)_2 (s)$		$-(400.52 \pm 1.66)$, ΔH_6

[a] The calorimetric solvent "S" is $2.0\ mol \cdot dm^{-3}$ HCl, $\sigma_a = \sqrt{\frac{\sum_{i=1}^{5} (x_i - \overline{x})^2}{n(n-1)}}$, in which n is the experimental number; x_i, a single value in a set of dissolution measurements; $\overline{x}$, the mean value of a set of measurement results

between the two solutions. The designed thermochemical cycle is correct and can be used to determine the standard molar enthalpy of formation of the title compound.

4 Conclusions

The crystal structure and low-temperature heat capacities of the complex, and the dissolution enthalpies of the reactants and product of a designed thermochemical reaction were reported. The standard molar enthalpy of formation of the title compound were calculated based on a reasonable thermochemical cycle. The enthalpy change of Eq. 5 was determined to be $-(64.275 \pm 0.461)\ kJ \cdot mol^{-1}$, which is an exothermic reaction. This shows that Eq. 5 is an enthalpy-driven process based on thermodynamic theory (Table 7).

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