Low-Temperature Heat Capacities and Standard Molar Enthalpy of Formation of Ethylenediammonium Tetrachlorocobaltate(II) Chloride $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2(s)$

Wen-Yan Dan,[†] You-Ying Di,*[,†] Chun-Ling Xin,[†] Yu-Xia Kong,[†] and Zhi-Cheng Tan[‡]

College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, Shandong Province, P.R. China, and Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P.R. China

A coordination compound, ethylenediammonium tetrachlorocobaltate(II) chloride $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2$, was synthesized by the method of liquid phase synthesis, in which ethylenediamine, cobalt chloride hexahydrate, and concentrated hydrochloric acid 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 complex were measured with a precise automated adiabatic calorimeter over the temperature range from (78 to 370) 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 of 298.15 K were calculated and tabulated at intervals of 5 K based on the fitted polynomial equation. A reasonable thermochemical cycle was designed, and the standard molar enthalpies of dissolution of the reactants and products of the synthesis reaction in the selected solvent were measured by an isoperibol solution-reaction calorimeter. The enthalpy change of the reaction was calculated to be $\Delta_r H_m^o = -(17.612 \pm 0.571)\ kJ \cdot mol^{-1}$ from the data of the standard molar enthalpies of dissolution. The standard molar enthalpy of formation of the title compund was determined to be $\Delta_f H_m^o\{(NH_3CH_2CH_2NH_3)_2[CoCl_4]Cl_2, s\} = -(1499.54 \pm 2.73)\ kJ \cdot mol^{-1}$ in accordance with Hess's law.

Introduction

Ethylenediamine is an important raw material in the chemical industry and pharmacy. It was used in the large-scale synthesis and application of medicines, emulsifiers, pesticides, ion exchange resins, and so on. It was also a hardening agent of epoxy resins used as adhesives and a good solvent for casein, albumin, and shell lac. In recent years, great attention has been paid to the complexation of ethylenediamine with many transition metals. Smith and Stratton[1] synthesized the title compound and investigated the crystal structure of the complex by a Picker FACS-I diffractometer. However, some important thermodynamic properties of the title compound, for example, low-temperature heat capacities and standard molar enthalpy of formation, have not been found in the literature, which restricted the progress of relevant theoretical studies and application development of the compounds. Heat capacity and standard molar enthalpy of formation of a substance are some of the most fundamental thermodynamic properties and are closely related to other physical, biological, physiological, and chemical properties.[2,3] 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 the present work is to measure low-temperature heat capacities of the compound by adiabatic calorimetry and determine the dissolution enthalpies of the reactants and products of the synthesis reaction by isoperibol solution-reaction calorimetry.

Experimental Section

Synthesis and Characterization of the Complex $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2$. Ethylenediammonium dichloride, cobalt chloride hexahydrate, and concentrated hydrochloric acid used as the reactants were of analytical grade with a labeled mass percent purity of more than 99.5 % and accurately weighed at the molar ratio of $n(CoCl_2 \cdot 6H_2O):n(ClH_3NCH_2CH_2NH_3Cl) = 1:2$. A certain amount of cobalt chloride hexahydrate (9.01528 g, about 38 mmol) was first dissolved in anhydrous ethanol, and an excess amount of concentrated hydrochloric acid was added. The corresponding stoichiometric ratio of ethylenediammonium dichloride was dissolved in anhydrous ethanol and added dropwise with stirring, and an exothermic reaction took place. The solution was heated and stirred in a 250 cm^3 flask under reflux for 6 h. The final solution was naturally cooled to room temperature and filtered, and the crude product was washed three times by anhydrous ethanol. The blue solid product was recrystallized using double-distilled water, and blue crystals were obtained. Finally, the sample was placed in a vacuum desiccator to dry in vacuum for 6 h. Theoretical contents of Co, C, Cl, H, and N in the compound have been calculated to be 14.89 %, 12.14 %, 53.73 %, 5.09 %, and 14.15 %, respectively. Chemical and elemental analysis (model: PE-2400, Perkin-Elmer, USA) have shown that the practical contents of Cl, C, H, and N in the compound have been measured to be 53.71 %, 12.12 %, 5.11 %, and 14.18 %, respectively. This showed the purity of the sample prepared was higher than 99.50

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* To whom correspondence may be addressed. Fax: +86-635-8239121. E-mail: diyouying@126.com, yydi@lcu.edu.cn.
[†] Liaocheng University.
[‡] Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

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Table 1. Crystal Data and Structure Refinement for $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2(s)$

crystallographic data	structure refinement
empirical formula	$C_4H_{20}Cl_6CoN_4$
formula weight	395.88
temperature	298(2) K
wavelength	0.71073 Å
crystal system	orthorhombic
space group	*Pnma*
unit cell dimensions	$a = 12.9074(12)$ Å, $b = 19.2887(18)$ Å, $c = 6.1772(5)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$
volume	1537.9(2) $Å^3$
Z	4
calculated density	1.710 $g \cdot cm^{-3}$
absorption coefficient	2.137 mm^{-1}
F(000)	804
crystal size	0.47 mm × 0.46 mm × 0.35 mm
θ range for data collection	2.11° to 25.02°
limiting indices	$-15 \leq h \leq 15$, $-22 \leq k \leq 17$, $-6 \leq l \leq 7$
reflections collected/unique	6709/1401 [R(int) = 0.0423]
completeness to θ = 24.99	99.9 %
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	1401/0/76
goodness-of-fit on F^2	1.001
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0242$, $wR_2 = 0.0549$
R indices (all data)	$R_1 = 0.0329$, $wR_2 = 0.0600$
extinction coefficient	0.0278(9)
largest diff. peak and hole	324 and −340 $e \cdot nm^{-3}$

%. The mass percent content of the chlorine in the complex was determined by gravimetry with AgCl.

X-ray Crystallography. A crystal with dimensions of 0.47 mm × 0.46 mm × 0.35 mm was glued to a fine glass fiber and was then mounted on the Bruker Smart 1000 CCD diffractometer with Mo Kα radiation, $\lambda = 0.71073$ Å. The intensity data were collected at 298(2) K. The structure was solved by direct methods and expanded using Fourier techniques with the SHELXL-97 program.[4] The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. The hydrogen atoms were added theoretically, which rode on the concerned atoms and were not refined. Crystal data and refinement details are summarized in Table 1.

Adiabatic Calorimetry. A precise automatic adiabatic calorimeter was used to measure heat capacities of the compound over the temperature range $78 \leq (T/K) \leq 370$. 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.[5] Briefly, the calorimeter mainly comprised 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 the middle shields, and between the middle and the outer shields, respectively, 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 applied 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 online 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 $78 \leq (T/K) \leq 400$. The sample mass used was 1.7143 g, which was equivalent to 0.0168 mol based on its molar mass, $M(Al_2O_3) = 101.9613\ g \cdot mol^{-1}$. The experimental molar heat capacities of α-Al_2O_3 were fitted by a least-squares method to a polynomial equation. Relative deviations of the experimental results from those of the smoothed curve were within ± 0.29 %, while the uncertainty is ± 0.30 %, as compared with the values given by the former National Bureau of Standards[6] 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 temperature have been corrected for heat exchange of the sample cell with its surroundings.[5] The sample mass used in the calorimetric measurements was 1.8134 g, which is equivalent to 0.0046 mol in terms of its molar mass, $M = 395.88\ g \cdot mol^{-1}$.

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.[7]

The thermistor was adopted as the sensor for controlling temperature in the thermostatic bath. However, the input signal of the modified high-precision temperature controller (model: DWT-702, manufactured by Shanghai No. 6 Automated Instrumentation Works), which worked in the PID (proportional−integral−derivative) mode, was not directly from the thermistor sensor, but from the signal of the self-made Wheatstone electric bridge used for temperature controlling. 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 temperature controlling of this kind of system can reach $\pm 1 \cdot 10^{-3}$ 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 controlling temperature system and another thermistor with a large negative temperature coefficient of resistance. The thermistor used as the 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 accuracy of 0.1 mK. The unbalanced voltage signal had 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 $\pm 1 \cdot 10^{-4}$ K at least 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

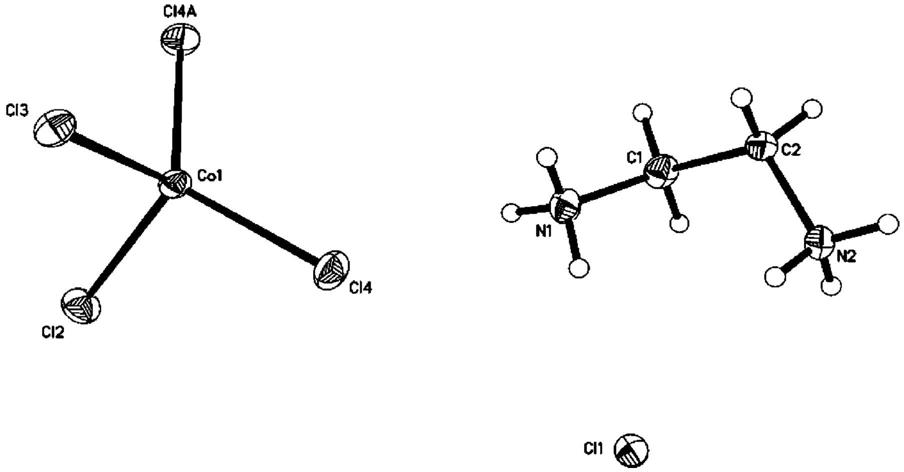

Figure 1. Structure of the title compound $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2$(s).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2(s)$[a]

Co(1)−Cl(4)	2.2664(7)	Cl(4)−Co(1)−Cl(4)#1	126.10(4)
Co(1)−Cl(4)#1	2.2664(6)	Cl(4)−Co(1)−Cl(2)	107.31(2)
Co(1)−Cl(2)	2.2866(10)	Cl(4)−Co(1)−Cl(3)	103.36(2)
Co(1)−Cl(3)	2.3167(10)	Cl(2)−Co(1)−Cl(3)	108.30(4)
N(1)−C(1)	1.480(3)	C(1)−N(1)−H(1A)	109.5
N(1)−H(1A)	0.8900	C(1)−N(1)−H(1B)	109.5
N(1)−H(1B)	0.8900	H(1A)−N(1)−H(1B)	109.5
N(1)−H(1C)	0.8900	C(2)−N(2)−H(2A)	109.5
N(2)−C(2)	1.477(3)	C(2)−N(2)−H(2B)	109.5
N(2)−H(2A)	0.8900	N(1)−C(1)−C(2)	113.4(2)
N(2)−H(2B)	0.8900	N(1)−C(1)−H(1D)	108.9
N(2)−H(2C)	0.8900	H(1D)−C(1)−H(1E)	107.7
C(1)−C(2)	1.502(4)	N(2)−C(2)−C(1)	113.3(2)
C(1)−H(1D)	0.9700	N(2)−C(2)−H(2D)	108.9
C(1)−H(1E)	0.9700	N(2)−C(2)−H(2E)	108.9
C(2)−H(2D)	0.9700	C(1)−C(2)−H(2E)	108.9
C(2)−H(2E)	0.9700	H(2D)−C(2)−H(2E)	107.7

[a] Symmetry transformations used to generate equivalent atoms: #1 x, $-y + 3/2$, z.

current through the heater was set at $I = 20.015$ mA, and the resistance of the electrical heater was $R = 1216.9\ \Omega$ at $T = 298.15$ K.

The reliability of the calorimeter was verified previously by measuring the dissolution enthalpy of KCl (calorimetric primary standard) in double-distilled water at $T = 298.15$ K. The mean dissolution enthalpy was $(17547 \pm 13)\ \mathrm{J \cdot mol^{-1}}$ for KCl, which compares with corresponding published data, $(17536 \pm 3.4)\ \mathrm{J \cdot mol^{-1}}$.[8]

In all dissolution experiments of the sample, 100 $\mathrm{cm^3}$ double-distilled water was chosen as the calorimetric solvent.

Results and Discussion

Crystal Structure. The molecular structure of $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2$(s) is shown in Figure 1. The selected bond lengths and angles of the title compound are listed in Table 2. The hydrogen bonds are listed in Table 3. Unit cell parameters are $a = 12.9074(12)$ Å, $b = 19.2887(18)$ Å, and $c = 6.1772(5)$ Å; $\alpha = \beta = \gamma = 90°$, respectively. It was found that the crystal structure of the coordination compound is orthorhombic, and the space group is *Pnma*, as shown in Table 1. Because the tetrahedral $[CoCl_4]^{2-}$ ion was located about the mirror plane, the whole molecular structure can be derived from symmetry operation. That is to say, Figure 1 was a part of the whole molecular structure. The cobalt atom was four-coordinate in the distorted tetrahedron geometry. The four chlorine atoms coordinated with the central cobalt atom. The coordination ion $[CoCl_4]^{2-}$, $[Cl]^-$, and ions $[H_3NCH_2CH_2NH_3]^{2+}$ are held together by electrovalent bonds. The crystal packing is dominated by an extended hydrogen-bonding network in Figure 2. In comparison with the literature,[1] it can be seen that the crystal data and the structure of the title compound determined were almost consistent with the reported results.

Low-Temperature Heat Capacities. The experimental molar heat capacities of the coordination compound are listed in Table 4 and plotted in Figure 3 and show that the heat capacity curve of the compound smoothly increased with temperature. The title compound was thermally stable over the temperature range between $T = (78 \text{ and } 370)$ K; no phase change, association, and thermal decomposition occurred. The experimental points in the temperature region between $T = 78$ K and $T = 370$ 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:

$$C_{p,\mathrm{m}}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 292.055 + 195.463X - 10.358X^2 + 5.017X^3 + 1.641X^4 \quad (1)$$

in which $X = (T/\mathrm{K} - 224)/146$. The coefficient of determination for the fitting R^2 equaled 0.99999. The value 224 is half of the upper limit of 370 K plus the lower limit of 78 K in the temperature range of (78 to 370) K, while 146 is half of the

Table 3. Hydrogen Bonds for $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2(s)$

D−H···A	d(D−H)/Å	d(H···A)/Å	DHA angle/deg	d(D···A)/Å	symmetry code of acceptor atom
N(1)−H(1A)···Cl(1)	0.890	2.372	157.44	3.212	/
N(1)−H(1B)···Cl(3)	0.890	2.350	173.34	3.235	$x, y, z + 1$
N(1)−H(1C)···Cl(2)	0.890	2.468	147.48	3.254	$x - 1/2, y, -z + 1/2$
N(2)−H(2A)···Cl(1)	0.890	2.436	145.92	3.212	$-x + 1, -y + 1, -z + 1$
N(2)−H(2A)···Cl(1)	0.890	2.840	124.19	3.420	/
N(2)−H(2B)···Cl(1)	0.890	2.373	158.28	3.217	$x - 1/2, y, -z + 3/2$
N(2)−H(2C)···Cl(1)	0.890	2.324	155.49	3.155	$-x + 1, -y + 1, -z + 2$

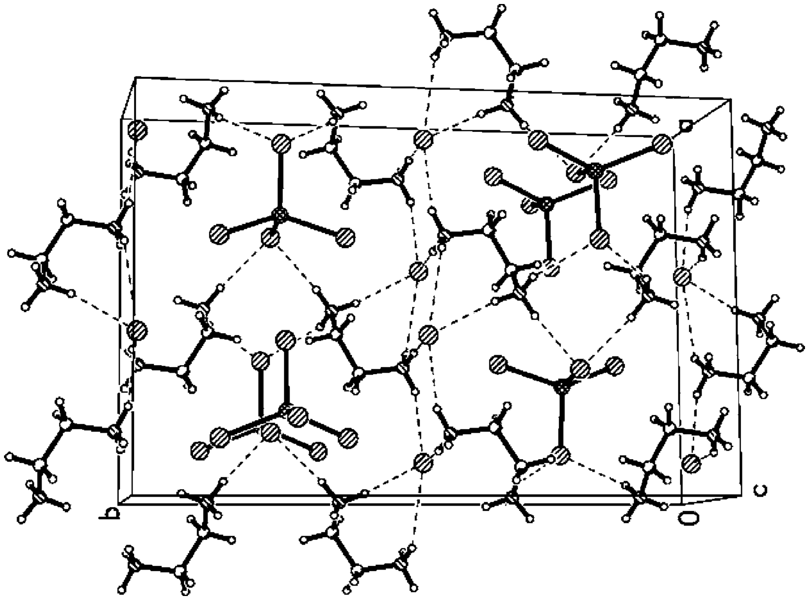

Figure 2. Packing of the structure of the title compound $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2(s)$ in a unit cell.

Table 4. Experimental Molar Heat Capacities of $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2(s)$

T / K	$C_{p,m}$ / $J\cdot K^{-1}\cdot mol^{-1}$	T / K	$C_{p,m}$ / $J\cdot K^{-1}\cdot mol^{-1}$	T / K	$C_{p,m}$ / $J\cdot K^{-1}\cdot mol^{-1}$
78.617	84.017	180.51	232.69	295.86	386.09
81.792	88.341	184.29	237.97	298.58	389.99
84.664	93.144	188.22	243.25	301.30	393.89
87.839	98.188	192.30	249.26	304.02	397.05
91.165	102.75	196.23	254.54	307.35	401.53
94.189	107.79	202.13	262.23	310.98	406.81
97.212	111.88	205.46	266.31	314.30	410.41
101.60	118.60	209.24	271.59	316.42	413.30
105.83	125.33	213.17	278.08	318.99	417.14
108.85	129.65	216.95	282.40	321.56	420.50
112.03	133.73	220.72	286.97	324.28	422.82
115.20	139.02	224.50	293.21	326.85	426.31
118.38	144.30	228.59	298.01	329.57	429.71
121.55	148.14	232.37	302.82	332.14	433.19
124.88	153.43	236.90	308.34	334.71	436.57
128.05	158.47	241.29	315.55	337.43	440.39
131.38	163.03	245.22	319.87	340.16	444.00
134.55	167.84	249.00	326.11	342.88	447.38
137.88	171.92	252.93	331.16	345.60	451.42
141.20	176.48	256.86	335.48	348.32	454.80
144.53	182.49	260.64	340.04	351.04	458.52
148.92	188.49	264.42	346.05	353.76	462.34
152.85	193.54	268.19	350.85	356.48	466.05
156.17	198.58	272.13	355.66	359.05	469.47
159.50	203.38	275.90	360.70	361.77	472.93
162.82	207.95	279.99	365.74	364.50	476.75
166.15	212.75	283.77	370.31	367.07	480.25
169.48	217.55	287.70	376.55	369.79	483.07
172.95	222.60	290.87	379.67		
176.58	227.88	293.14	382.65		

upper limit of 370 K minus the lower limit of 78 K in the same range. The reduced temperature (X) obtained using the method is 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 of X in the fitted polynomial equation according to the principle in statistics.

Equation 1 is valid over a temperature range of (78 to 370) K. The relative deviations of the smoothed heat capacities obtained by the above equation from experimental heat capacities were within ± 0.40 % except for one experimental point at $T = 112.03$ K.

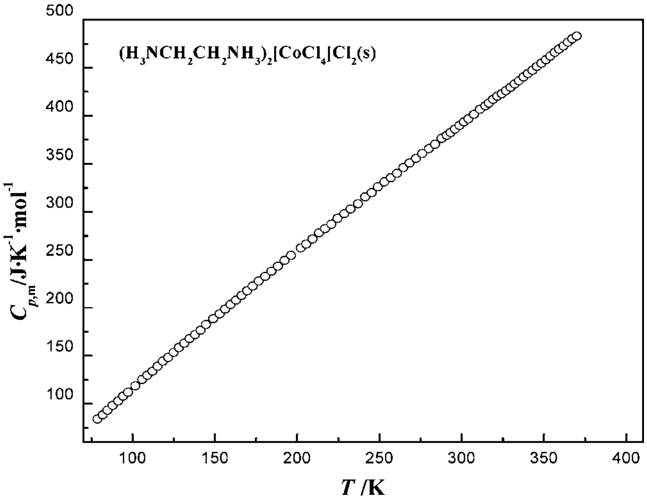

Figure 3. Curve of experimental molar heat capacities of the title complex against the absolute temperature.

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,

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

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

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

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

Table 5. Smoothed Heat Capacities and Thermodynamic Functions of $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2(s)$

T / K	$C_{p,m}$ / $J\cdot K^{-1}\cdot mol^{-1}$	$H_T - H_{298.15\ K}$ / $kJ\cdot mol^{-1}$	$S_T - S_{298.15\ K}$ / $J\cdot K^{-1}\cdot mol^{-1}$	$G_T - G_{298.15\ K}$ / $kJ\cdot mol^{-1}$
80	85.932	−52.848	−275.96	−30.771
85	93.593	−52.399	−270.52	−29.405
90	101.22	−51.912	−264.95	−28.066
95	108.80	−51.387	−259.28	−26.755
100	116.35	−50.824	−253.51	−25.473
105	123.87	−50.223	−247.65	−24.220
110	131.34	−49.585	−241.72	−22.996
115	138.78	−48.910	−235.72	−21.802
120	146.17	−48.197	−229.65	−20.639
125	153.54	−47.448	−223.53	−19.506
130	160.86	−46.662	−217.37	−18.404
135	168.14	−45.840	−211.16	−17.333
140	175.39	−44.981	−204.91	−16.293
145	182.60	−44.086	−198.63	−15.285
150	189.78	−43.155	−192.31	−14.307
155	196.92	−42.188	−185.97	−13.362
160	204.02	−41.186	−179.61	−12.448
165	211.09	−40.148	−173.22	−11.566
170	218.12	−39.075	−166.82	−10.715
175	225.12	−37.967	−160.40	−9.8972
180	232.08	−36.824	−153.96	−9.1111
185	239.02	−35.646	−147.51	−8.3571
190	245.92	−34.433	−141.04	−7.6354
195	252.79	−33.187	−134.57	−6.9461
200	259.62	−31.906	−128.08	−6.2892
205	266.43	−30.590	−121.59	−5.6648
210	273.21	−29.241	−115.09	−5.0730
215	279.97	−27.858	−108.58	−4.5137
220	286.69	−26.442	−102.07	−3.9871
225	293.39	−24.991	−95.548	−3.4931
230	300.07	−23.508	−89.026	−3.0318
235	306.73	−21.991	−82.501	−2.6032
240	313.36	−20.441	−75.972	−2.2073
245	319.97	−18.857	−69.442	−1.8441
250	326.57	−17.241	−62.909	−1.5135
255	333.14	−15.592	−56.376	−1.2157
260	339.70	−13.910	−49.843	−0.95045
265	346.25	−12.195	−43.309	−0.71786
270	352.78	−10.447	−36.775	−0.51789
275	359.31	−8.6668	−30.241	−0.35050
280	365.82	−6.8539	−23.708	−0.21569
285	372.33	−5.0086	−17.176	−0.11345
290	378.83	−3.1306	−10.644	−0.043770
295	385.33	−1.2202	−4.1138	−0.0066500
298.15	389.42	0	0	0
300	391.82	0.72266	2.4159	−0.0021100
302	394.42	1.5089	5.0276	−0.0094200
310	404.82	4.7059	15.473	−0.090845
315	411.32	6.7463	22.001	−0.18418
320	417.83	8.8192	28.529	−0.31020
325	424.35	10.925	35.057	−0.46897
330	430.88	13.063	41.586	−0.66050
335	437.43	15.234	48.115	−0.88485
340	443.99	17.437	54.645	−1.1420
345	450.56	19.674	61.176	−1.4320
350	457.16	21.943	67.708	−1.7548
355	463.79	24.245	74.241	−2.1104
360	470.43	26.581	80.776	−2.4985
365	477.11	28.950	87.312	−2.9190
370	483.82	31.352	93.848	−3.3716

Enthalpy Change of the Synthesis Reaction of the Complex. The synthesis reaction is shown in the following chemical equation:

$$2ClH_3NCH_2CH_2NH_3Cl(s) + CoCl_2\cdot 6H_2O(s) = (H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2(s) + 6H_2O(l) \quad (5)$$

The standard molar enthalpy of dissolution of the reactants and products in reaction 5 were measured by an isoperibol solution calorimeter. The enthalpy change of eq 5 can be calculated from these standard molar enthalpies of dissolution. Finally, the standard molar enthalpy of formation of the complex was determined in accordance with Hess's law.

First, ethylenediammonium dichloride (analytical grade with a labeled mass percent purity of more than 99.5 %) was dried for 6 h at $T = 323$ K in a vacuum desiccator. It was ground within an agate mortar into fine powder. About 0.133 g or 2 mmol of ethylenediammonium dichloride was dissolved in 100 cm^3 of double-distilled water at $T = 298.15$ K. The final solution obtained was named as solution A_1. The experimental results of the process are listed in Table 6, in which "S" represented 100 cm^3 of double-distilled water. The dissolution process of the ethylenediammonium chloride in double-distilled water was expressed as follows:

$$\{ClH_3NCH_2CH_2NH_3Cl(s)\} + S = \text{solution } A_1$$

A certain amount of $CoCl_2\cdot 6H_2O(s)$ was weighed at a mole ratio of $n(ClH_3NCH_2CH_2NH_3Cl){:}n(CoCl_2\cdot 6H_2O) = 2{:}1$. The experimental results are listed in Table 6. The dissolution process of $CoCl_2\cdot 6H_2O(s)$ in solution A_1 was expressed as follows:

$$\{CoCl_2\cdot 6H_2O(s)\} + \text{solution } A_1 = \text{solution A}$$

The product $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2(s)$ was also ground within an agate mortar into a fine powder. A certain amount of the title compound was weighed in accordance with the stoichiometric coefficient of the reactants and products in eq 5. The dissolution process of $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2(s)$ in 100 cm^3 of double-distilled water was expressed as follows:

$$\{(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2(s)\} + S = \text{solution B}$$

The detailed results obtained from five tests have been listed in Table 6.

In addition, the dilution enthalpy of the product $\{6H_2O(l)\}$ in eq 5 is within the scope of the experimental error, cannot be measured, and may be omitted.

The enthalpy change of eq 5 is calculated in accordance with the thermochemical cycle and the experimental results as follows,

$$\begin{aligned}\Delta_r H_m^o(5) &= \sum \Delta_s H^o_{m(\text{Reactants})} - \sum \Delta_s H^o_{m(\text{Products})}\\ &= 2\Delta H_1 + \Delta H_2 - \Delta H_3\\ &= 2\cdot 20.411 + 2.743 - 61.177\\ &= -(17.612 \pm 0.571)\ kJ\cdot mol^{-1}\end{aligned}$$

Standard Molar Enthalpy of Formation of the Complex. A reaction scheme used to determine the standard molar enthalpy of formation of $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2(s)$ is given in Table 7. The enthalpy change of the liquid phase reaction 5 was combined with other auxiliary thermodynamic data of $\Delta_f H_m^o(ClH_3NCH_2CH_2NH_3Cl, s) = -(540.74 \pm 1.33)\ kJ\cdot mol^{-1}$,[9] $\Delta_f H_m^o(CoCl_2\cdot 6H_2O, s) = -2115.43\ kJ\cdot mol^{-1}$,[10] $\Delta_f H_m^o(H_2O, l) = -(285.83 \pm 0.04)\ kJ\cdot mol^{-1}$,[11] to derive the standard molar enthalpy of formation of the title compound $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2(s)$:

$$\begin{aligned}\Delta_f H_m^o\{(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2, s\} &= \Delta H_7\\ &= \Delta_r H_m^o(5) + 2\Delta_f H_m^o(ClH_3NCH_2CH_2NH_3Cl, s) + \\ &\quad \Delta_f H_m^o(CoCl_2 \cdot 6H_2O, s) - 6\Delta_f H_m^o(H_2O, l)\\ &= 2\,\Delta H_1 + \Delta H_2 - \Delta H_3 + 2\Delta H_4 + \Delta H_5 - 6\Delta H_6\\ &= -(1499.54 \pm 2.73)\ \mathrm{kJ \cdot mol^{-1}}\end{aligned}$$

in which ΔH_1 to ΔH_7 were the enthalpy changes of the reactions corresponding to the number of reactions in Table 7.

In this paper, all of the reactants and products 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 Figure 4. The experimental values of the refractive indexes of solution A and solution B were measured to be (1.3332 ± 0.0002) and (1.3330 ± 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 between the two solutions.

Conclusions

The enthalpy change of the synthesis reaction, eq 5, was determined to be $-(17.612 \pm 0.571)\ \mathrm{kJ \cdot mol^{-1}}$. Apparently, the reaction is exothermic. It showed that the reaction was an enthalpy-driven process. On the other hand, all of the reactants were solid, and the products included one solid and one liquid. It could be concluded from an increase of degree

Table 6. Dissolution Enthalpies of Reactants and Products in Reaction 5 in the Selected Solvents at $T = 298.15$ K[a]

system	solvent	avg $\Delta_s H_m^o$ / kJ·mol^{-1}	no.	m / g	$\Delta E_s/\Delta E_e$	t_e / J	Q_s / J	$\Delta_s H_m^o$ / kJ·mol^{-1}
ethylenediammonium chloride	double-distilled water	20.411 ± 0.214	1	0.26634	−1.1854	72.656	41.986	20.969
			2	0.26655	−1.1743	71.562	40.966	20.444
			3	0.26630	−1.1720	71.968	41.118	20.539
			4	0.26627	−1.1183	72.141	39.328	19.647
			5	0.26651	−1.1522	72.969	40.986	20.457
cobalt chloride hexahydrate	solution A_1	2.743 ± 0.071	1	0.23741	−0.4155	14.203	2.8768	2.8832
			2	0.23725	−1.6625	3.359	2.8094	2.7223
			3	0.23780	−0.9581	6.015	2.8053	2.8109
			4	0.23712	−0.8030	7.187	2.8134	2.8230
			5	0.23758	−0.6032	8.421	2.4762	2.4798
ethylenediammonium tetrachlorocobaltate (II) chloride	double-distilled water	61.177 ± 0.372	1	0.39519	−1.2364	101.390	61.1111	61.1405
			2	0.39515	−1.1922	102.938	59.8261	59.9366
			3	0.39545	−1.1481	108.765	60.8744	60.9406
			4	0.39579	−1.2708	99.750	61.7954	61.8094
			5	0.39542	−1.5415	82.485	61.9847	62.0568

[a] 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; $\Delta_s H_m^o = Q_s/n = -(\Delta E_s/\Delta E_e)\cdot I^2 R t_e(M/m)$, where R is the electroresistance ($R = 1216.9\ \Omega$ at $T = 298.15$ K), I is the current ($I = 20.015$ mA), and M is molar mass of the sample.

Table 7. Reaction Scheme Used to Determine the Standard Molar Enthalpy of Formation of Ethylenediammonium Tetrachlorocobaltate(II) Chloride

no.	reactions	formed solution	$\Delta_f H_m^o$ or $(\Delta_s H_m^o \pm \sigma_a)$[a] / kJ·mol^{-1}
1	$\{ClH_3NCH_2CH_2NH_3Cl(s)\} + S =$	A_1	20.411 ± 0.214, ΔH_1
2	$\{CoCl_2 \cdot 6H_2O(s)\} + \text{solution } A_1 =$	A	2.743 ± 0.071, ΔH_2
3	$\{(H_3NCH_2CH_2NH_3)_2CoCl_6(s)\} + S =$	B	61.177 ± 0.372, 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	$Cl_2(g) + 3H_2(g) + 3O_2(g) + Co(s) = CoCl_2 \cdot 6H_2O(s)$		−2115.43, ΔH_5
6	$H_2(g) + 1/2O_2(g) = H_2O(l)$		−(285.83 ± 0.04), ΔH_6
7	$4C(s) + 10H_2(g) + 2N_2(g) + 3Cl_2(g) + Co(s) = C_4H_{20}Cl_6CoN_4(s)$		−(1499.54 ± 2.73), ΔH_7

[a] The calorimetric solvent S is 100 cm^3 of double-distilled water; $\sigma_a = [\sum_{i=1}^{5} (x_i - \bar{x})^2/n(n-1)]^{1/2}$, in which n is the experimental number; x_i, a single value in a set of dissolution measurements; $\bar{x}$, the mean value of a set of measurement results.

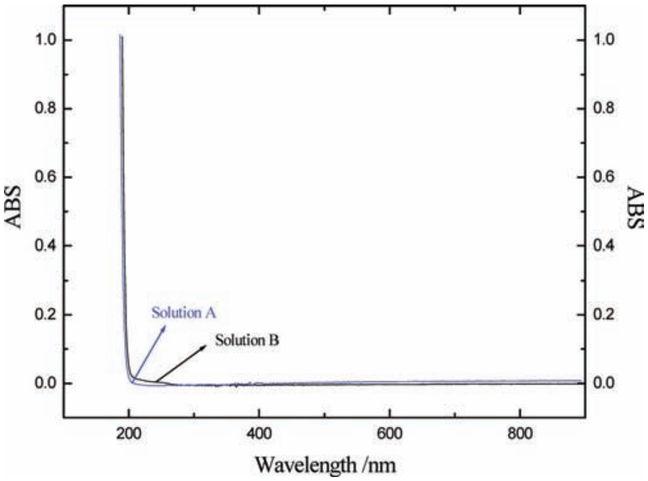

Figure 4. UV−vis spectra of solution A obtained from the dissolution of the reactants and solution B from dissolution of the products (diluted to 1:20).

of disorder in the reaction that the entropy change of the reaction should be more than zero according to the statistical explanation of the entropy of the system in statistical thermodynamics. Therefore, the reaction may be an entropy-driven process. In addition, the standard molar enthalpy of formation of the title compound $(H_3NCH_2CH_2NH_3)_2[CoCl_4]Cl_2$ was negative with a large absolute value, which showed that it has lower energy and a more stable structure in comparison with the stable elementary substance from which it was made.

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