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Crystal Structures, Lattice Potential Energies, and Thermochemical Properties of Crystalline Compounds $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, 12, and 13)

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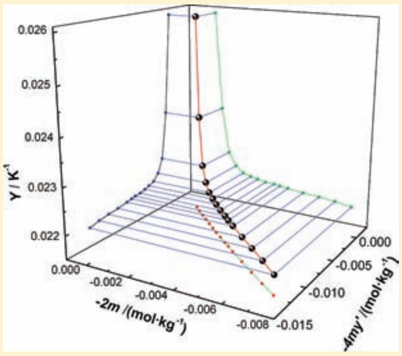
S *Supporting Information*

ABSTRACT: As part of our ongoing project involving the study of $(1\text{-}C_nH_{2n+1}NH_3)_2MCl_4(s)$ (where M is a divalent metal ion and n = 8−18), we have synthesized the compounds $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, 12, and 13), and the details of the structures are reported herein. All of the compounds were crystallized in the monoclinic form with the space group $P2_1/n$ for $(1\text{-}C_8H_{17}NH_3)_2ZnCl_4(s)$, $P2_1/c$ for $(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4(s)$, $P2_1/c$ for $(1\text{-}C_{12}H_{25}NH_3)_2ZnCl_4(s)$, and $P2_1/m$ for $(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4(s)$. The lattice potential energies and ionic volumes of the cations and the common anion of the title compounds were obtained from crystallographic data. Molar enthalpies of dissolution of the four compounds at various molalities were measured at 298.15 K in the double-distilled water. According to Pitzer's theory, molar enthalpies of dissolution of the title compounds at infinite dilution were obtained. Finally, using the values of molar enthalpies of dissolution at infinite dilution ($\Delta_sH_m^\infty$) and other auxiliary thermodynamic data, the enthalpy change of the dissociation of $[ZnCl_4]^{2-}(g)$ for the reaction $[ZnCl_4]^{2-}(g) \rightarrow Zn^{2+}(g) + 4Cl^-(g)$ was obtained, and then the hydration enthalpies of cations were calculated by designing a thermochemical cycle.



■ INTRODUCTION

This paper is one of a series of investigations[1−3] about the crystal structures, lattice potential energies, and thermochemical properties of crystalline compounds bis-*n*-alkylammonium tetrachlorometallates $(1\text{-}C_nH_{2n+1}NH_3)_2MCl_4(s)$ (where M is a divalent metal ion and n = 8−18), which are kinds of solid−solid phase change materials (SSPCMs).[4,5] In past decades, these compounds have been extensively investigated, as they show a variety of magnetic phase transitions such as a small change in volume, no volatilization, low temperature, and high enthalpy of solid−solid phase transition.[6,7] In our previous work, we have focused on crystal structures and phase transitions of these compounds. In this paper, we are extending our investigations to thermodynamic properties of $(1\text{-}C_nH_{2n+1}NH_3)_2MCl_4(s)$ as kinds of aqueous electrolytes at T = 298.15 K, which are needed to develop their new application fields and to carry out relevant theoretical research.

In this work, a series of crystalline compounds $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, 12, and 13) are synthesized using the method of liquid phase reaction. X-ray crystallography is applied to characterize crystal structures of the compounds. Ionic volumes of $[ZnCl_4]^{2-}$ and $[1\text{-}C_nH_{2n+1}NH_3]^+$ are derived from crystallographic data, and molar enthalpies of dissolution of $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, 12, and 13) at different concentrations are determined using an isoperibol solution-reaction calorimeter. Since $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ may be dissociated to $\{2[1\text{-}C_nH_{2n+1}NH_3]^+(aq) + Zn^{2+}(aq) + 4Cl^-(aq)\}$ in water and molalities of the samples in the dissolution experiment are relatively low in the present research, each electrolyte solution may be regarded as an unsymmetrical mixed electrolytes solution: $2(1\text{-}C_nH_{2n+1}NH_3Cl)\text{-}ZnCl_2$ and $m_{[1\text{-}C_nH_{2n+1}NH_3]^+} = 2m$, $m_{Zn^{2+}} = m$, and $m_{Cl^-} = 4m$. The method of practical application of an unsymmetrical mixed electrolytes solution of realistic concentration has been extensively investigated both theoretically and experimentally by Pitzer et al.[8−10] According to Pitzer's electrolyte solution theory, molar enthalpies of dissolution of the title compounds at infinite dilution are determined. The sums of Pitzer's parameters $(4\beta^{(0)L}_{1\text{-}C_nH_{2n+1}NH_3,Cl} + 2\beta^{(0)L}_{Zn,Cl} + \theta^{L}_{1\text{-}C_nH_{2n+1}NH_3,Zn})$ and $(2\beta^{(1)L}_{1\text{-}C_nH_{2n+1}NH_3,Cl} + \beta^{(1)L}_{Zn,Cl})$ are obtained, and the dissociation enthalpy of $[ZnCl_4]^{2-}(g)$ and hydration enthalpies of $[1\text{-}C_nH_{2n+1}NH_3]^+$ can be calculated from molar enthalpies of dissolution of the title compounds at infinite dilution with other auxiliary thermodynamic quantities through a thermodynamic cycle.

■ EXPERIMENTAL SECTION

Preparation of the Title Compounds. $1\text{-}C_nH_{2n+1}NH_2$ (n = 8, 10, 12, and 13), hydrochloric acid (0.37 in mass fraction), and zinc

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Table 1. Results of Chemical Analysis, Elemental Analysis, and Purities of the Title Compounds

Sample		$(1\text{-}C_8H_{17}NH_3)_2ZnCl_4$	$(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4$	$(1\text{-}C_{12}H_{25}NH_3)_2ZnCl_4$	$(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4$
calculated	C	41.09%	45.86%	49.71%	51.36%
	H	8.62%	9.24%	9.73%	9.95%
	N	5.99%	5.35%	4.83%	4.61%
	Zn	13.98%	12.49%	11.28%	10.76%
	Cl	30.32%	27.07%	24.45%	23.32%
found	C	41.20%	45.71%	49.61%	51.41%
	H	8.59%	9.26%	9.77%	9.91%
	N	5.96%	5.37%	4.85%	4.63%
	Zn	13.94%	12.53%	11.25%	10.81%
	Cl	30.31%	27.13%	24.52%	23.24%
purity		99.50%	99.63%	99.59%	99.54%

Table 2. Crystallographic Data and Structure Refinement for $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, and 13)

empirical formula	$(1\text{-}C_8H_{17}NH_3)_2ZnCl_4$	$(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4$	$(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4$
fw	467.67	523.77	607.93
temp/K	298(2)	298(2)	298(2)
wavelength/Å	0.71073	0.71073	0.71073
cryst syst, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/c$	monoclinic, $P2_1/m$
unit cell dimensions/(Å or deg)	a = 7.3729(8)	a = 7.3785(9)	a = 10.6300(10)
	b = 10.3435(11)	b = 10.2970(11)	b = 7.3041(8)
	c = 32.512(3)	c = 37.695(3)	c = 43.984(4)
	$\alpha = \gamma$ = 90	$\alpha = \gamma$ = 90	$\alpha = \gamma$ = 90
	β = 95.3270(10)	β = 95.5490(10)	β = 94.2900(10)
volume/Å^3	2468.7(4)	2850.5(5)	3405.5(6)
Z, calcd density/g·cm^{-3}	4, 1.258	4, 1.220	4, 1.186
absorption coeff/mm^{-1}	1.429	1.245	1.051
F(0 0 0)	992	1120	1312
cryst size/mm^3	0.45 × 0.41 × 0.23	0.45 × 0.20 × 0.17	0.48 × 0.26 × 0.13
Θ range for data collection	2.07−25.02°	2.56−25.00°	1.92−25.02°
limiting indices	$-8 \leq h \leq 5, -12 \leq k \leq 11,$ $-36 \leq l \leq 38$	$-7 \leq h \leq 8, -12 \leq k \leq 10,$ $-44 \leq l \leq 44$	$-12 \leq h \leq 12, -8 \leq k \leq 8,$ $-52 \leq l \leq 43$
reflns collected/unique	12063/4346 [R(int) = 0.0534]	13898/5012 [R(int) = 0.0606]	16556/6288 [R(int) = 0.0560]
completeness to Θ = 25.02/25.00/24.98	99.9%	99.7%	96.2%
absorption correction	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents
max. and min transmission	0.7346 and 0.5656	0.8163 and 0.6043	0.8755 and 0.6324
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	4346/0/208	5012/0/248	6288/0/457
goodness-of-fit on F^2	1.150	1.080	1.106
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0653, wR_2 = 0.1434	R_1 = 0.0674, wR_2 = 0.1409	R_1 = 0.1495, wR_2 = 0.2763
R indices (all data)	R_1 = 0.0943, wR_2 = 0.1562	R_1 = 0.1185, wR_2 = 0.1636	R_1 = 0.1792, wR_2 = 0.2895
largest diff. peak and hole/e·Å^{-3}	0.383 and −0.601	0.539 and −0.477	0.983 and −1.294

chloride (0.999 in mass fraction) used as the reactants and anhydrous ethyl alcohol chosen as the solvent are all of analytical grade. The masses of reactants are accurately weighed at the molar ratio of 2:2:1 for $n(1\text{-}C_nH_{2n+1}NH_2)/n(HCl)/n(ZnCl_2)$. A certain amount of $1\text{-}C_nH_{2n+1}NH_2$ is first dissolved into anhydrous ethyl alcohol in a 100 cm^3 flask. Zinc chloride is added slowly under sufficient stirring, and then hydrochloric acid is added drop by drop. The mixtures are heated and stirred under reflux for 6 h. When the final solutions are cool, they are filtered. Colorless single crystals suitable for X-ray diffraction are obtained one week later by slow evaporation. The products are recrystallized three times with anhydrous ethyl alcohol, and colorless crystals are gained. Finally, the samples are placed in a vacuum desiccator at T = 303.15 K to dry in a vacuum for 12 h; the final products are placed in weighing bottles and preserved in a desiccator. The mass fraction purities of Zn and Cl in the compounds are determined by chemical analysis. C, H, and N are determined using element analysis (model: PE-2400, Perkin-Elmer, USA). The values of the relative data are listed in Table 1.

Caution! *Hydrochloric acid (0.37 in mass fraction), zinc chloride, and* $1\text{-}C_nH_{2n+1}NH_2$ *(n = 8, 10, 12, and 13) used in this study are strongly corrosive and therefore should be handled with care in small quantities.*

X-Ray Crystallography. The crystals are glued to fine glass fibers and then mounted on a Bruker Smart-1000 CCD diffractometer with

Mo Kα radiation, λ = 0.71073 Å. The intensity data are collected in the $\varphi-\omega$ scan mode at T = (298 ± 2) K. The empirical absorption corrections are based on multi-scan. The structures are solved by direct methods and difference Fourier syntheses, and all non-hydrogen atoms are refined anisotropically on F^2 using the full-matrix least-squares method. All calculations are performed with the program package SHELXTL.[11,12]

The crystal data and structure refinement for the compounds are summarized in Table 2. We have applied for the CCDC numbers 823691 for $(1\text{-}C_8H_{17}NH_3)_2ZnCl_4(s)$, 823693 for $(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4(s)$, and 823692 for $(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4(s)$.

Isoperibol Solution-Reaction Calorimeter. The isoperibol solution-reaction calorimeter consists primarily of a precision temperature controlling system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precision temperature measuring system, and a data acquisition and processing system. During whole experiments, the water thermostat is automatically maintained at T = 298.15 K, and the maximum variation is found to be $\pm 1 \times 10^{-3}$ K. Experiments have demonstrated that the precision of measuring the temperature can reach $\pm 1 \times 10^{-4}$ K. The principle and structure of the calorimeter are described in detail elsewhere.[13,14]

The reliability of the calorimeter was verified previously by measuring the dissolution enthalpy of KCl (calorimetrically primary standard) in double-distilled water. According to the molar ratio of KCl to water, $n_{KCl}/n_{H_2O} \approx 1{:}1110$, a certain amount of KCl is dissolved in 100 cm^3 of double-distilled water at T = 298.150 ± 0.001 K. The average enthalpy of dissolution of KCl is 17547 ± 13 J·mol^{-1}, which compares with corresponding published data, 17536 ± 3.4 J·mol^{-1}, under the same experimental conditions.[15] Experiments demonstrate that the uncertainty between the measuring value and the literature value is within ±0.3%.

RESULTS AND DISCUSSION

Description of Crystal Structures. We investigated the crystal structure of $(1\text{-}C_{12}H_{25}NH_3)_2ZnCl_4(s)$ using X-ray crystallography in 2010.[3] In the present work, X-ray crystallography is applied to characterize the crystal structures of the other three compounds. The crystal parameters, data collections, and refinement results for the compounds are listed in Table 2. It is found from Table 2 and our previous work[3] that crystal structures of $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, 12, and 13) are all monoclinic, and Z = 4. And space groups of the four compounds are $P2_1/n$, $P2_1/c$, $P2_1/c$, and $P2_1/m$, respectively. The selected bond lengths and angles of $(1\text{-}C_8H_{17}NH_3)_2ZnCl_4$, $(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4$, and $(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4$ are listed in Table 3. The information on hydrogen bonds is given in Table 4. The molecular structures of $(1\text{-}C_8H_{17}NH_3)_2ZnCl_4$, $(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4$, and $(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4$ are shown in Figures 1, 2, and 3, respectively. As shown in Figure 4−6, the $[ZnCl_4]^{2-}$ anion is connected with $[1\text{-}C_nH_{2n+1}NH_3]^+$ cations through electrostatic interaction and hydrogen bonds.

By comparison of the crystal data of $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, 12, and 13), it can be seen that unit cell dimensions of the four compounds are very close. The Zn atom for each compound is bound tetrahedrally by four chlorine atoms to form a slightly distorted tetrahedron. The C−N distances of $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, 12, and 13) are nearly equal, lying in the range 1.388(11)−1.469(8) Å, and shorter than the normal mean bond distances (1.52 Å).[16] The Cl−Zn−Cl bond angles range from 105.43(6) to 111.57(6)° and deviate from the regular tetrahedron angle of 109.28°. The difference between them is caused mainly due to the forming of hydrogen bonds. These results reveal that the interactions of hydrogen bonds play a critical role in formation, stability, and crystallization of the cluster, and the hydrogen bonds N−H···Cl as well as the van der Waals forces exist in the crystals to stabilize the structures.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, and 13)

selected bonds	bond lengths (Å)	selected angles	bond angles (deg)
	$(1\text{-}C_8H_{17}NH_3)_2ZnCl_4(s)$		
Zn(1)−Cl(1)	2.2504(15)	Cl(1)−Zn(1)−Cl(2)	111.57(6)
Zn(1)−Cl(2)	2.2727(16)	Cl(1)−Zn(1)−Cl(3)	108.23(6)
Zn(1)−Cl(3)	2.2659(15)	Cl(3)−Zn(1)−Cl(2)	105.43(6)
Zn(1)−Cl(4)	2.2401(17)	Cl(4)−Zn(1)−Cl(2)	109.81(6)
N(1)−C(1)	1.455(7)	Cl(4)−Zn(1)−Cl(1)	111.39(7)
N(2)−C(9)	1.466(7)	Cl(4)−Zn(1)−Cl(3)	110.24(7)
	$(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4(s)$		
Zn(1)−Cl(1)	2.2539(18)	Cl(1)−Zn(1)−Cl(2)	111.29(7)
Zn(1)−Cl(2)	2.2803(17)	Cl(1)−Zn(1)−Cl(3)	108.46(7)
Zn(1)−Cl(3)	2.2702(18)	Cl(3)−Zn(1)−Cl(2)	105.57(7)
Zn(1)−Cl(4)	2.2405(19)	Cl(4)−Zn(1)−Cl(1)	111.36(8)
N(1)−C(1)	1.459(8)	Cl(4)−Zn(1)−Cl(2)	109.79(7)
N(2)−C(11)	1.469(8)	Cl(4)−Zn(1)−Cl(3)	110.20(8)
	$(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4(s)$		
Zn(1)−Cl(1)	2.246(2)	Cl(2)−Zn(1)−Cl(1)	109.69(10)
Zn(1)−Cl(2)	2.235(3)	Cl(3)−Zn(1)−Cl(1)	111.06(6)
Zn(1)−Cl(3)	2.248(2)	Cl(2)−Zn(1)−Cl(3)	108.35(7)
Zn(2)−Cl(4)	2.225(3)	Cl(4)−Zn(2)−Cl(5)	109.51(11)
N(1)−C(1)	1.388(11)	Cl(4)−Zn(2)−Cl(6)	108.16(7)
N(2)−C(14)	1.390(13)	Cl(6)−Zn(2)−Cl(5)	111.31(7)

Lattice Potential Energies. A remarkably successful empirical equation is used to estimate lattice potential energies for the general type of the salts of M_pX_q:[17]

$$U_{POT} = |z_+||z_-|\nu(\alpha'/V_m^{1/3} + \beta') \tag{1}$$

where z_+ and z_- are the respective charges on the cation and anion of a compound and ν is the number of ions per molecule and equals ($p + q$). For the case of salts of formula M_2X with a charge ratio of 1:2, such as $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, 12, and 13), $z_+ = 1$, $z_- = 2$, $p = 2$, $q = 1$, $\nu = 3$, $\alpha' = 165.3$ kJ·mol^{-1}·nm, $\beta' = -29.8$ kJ·mol^{-1}, and V_m is in units of nm^3:[17]

$$V_m(\text{nm}^3) = M_m/\rho N_A = 1.66045 \times 10^{-3} M_m/\rho \tag{2}$$

where N_A is Avogadro's constant, 6.02245×10^{23} molecule·mol^{-1}. Thus, formula 1 is changed to[3,17]

$$U_{POT} = \gamma(\rho/M_m)^{1/3} + \delta \tag{3}$$

where the values of the constants for M_2X (1:2) are γ = 8375.6 kJ·mol^{-1}·cm and δ = −178.8 kJ·mol^{-1}.[18] The density ρ/(g·cm^{-3}) and molar mass M_m/(g·mol^{-1}) are obtained from the crystal structure data of the title compounds in Table 2. V_m can be calculated according to eq 2; consequently, lattice potential energies of $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, and 13) are derived. The results of lattice potential energies and molecular volumes of the title compounds are listed in Table 5.

The lattice potential energy of $(1\text{-}C_{12}H_{25}NH_3)_2ZnCl_4(s)$ was derived to be 888.82 kJ·mol^{-1} by us in 2010. In comparison with

Table 4. Hydrogen Bond Lengths (Å) and Bond Angles (deg) for $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, and 13)

D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
$(1\text{-}C_8H_{17}NH_3)_2ZnCl_4(s)$				
N(1)−H(1C)···Cl(2)	0.89	2.44	3.281(5)	157.6
N(1)−H(1C)···Cl(4)	0.89	2.83	3.274(5)	112.0
N(2)−H(2C)···Cl(2)	0.89	2.50	3.355(5)	160.1
N(2)−H(2C)···Cl(3)	0.89	2.95	3.447(5)	117.3
N(1)−H(1A)···Cl(3)#1	0.89	2.64	3.306(5)	132.6
N(1)−H(1A)···Cl(4)#1	0.89	2.98	3.743(5)	144.6
N(1)−H(1B)···Cl(1)#2	0.89	2.67	3.437(5)	145.6
N(2)−H(2A)···Cl(3)#3	0.89	2.48	3.303(5)	153.4
N(2)−H(2B)···Cl(1)#4	0.89	2.41	3.266(5)	161.3
symmetry code: #1 $-x + 1, -y + 1, -z + 1$; #2 $-x, -y + 1, -z + 1$; #3 $-x + 1, -y + 2, -z + 1$; #4 $x + 1, y, z$				
$(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4(s)$				
N(1)−H(1C)···Cl(2)	0.89	2.38	3.252(6)	165.5
N(2)−H(2C)···Cl(2)	0.89	2.49	3.349(6)	162.6
N(1)−H(1A)···Cl(3)#1	0.89	2.58	3.319(6)	140.3
N(1)−H(1B)···Cl(1)#2	0.89	2.72	3.436(6)	138.5
N(2)−H(2A)···Cl(3)#3	0.89	2.49	3.306(6)	153.6
N(2)−H(2B)···Cl(1)#4	0.89	2.40	3.258(6)	163.0
symmetry code: #1 $-x + 1, -y + 1, -z + 1$; #2 $-x + 2, -y + 1, -z + 1$; #3 $-x + 1, -y, -z + 1$; #4 $x - 1, y, z$				
$(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4(s)$				
N(2)−H(2C)···Cl(6)	0.89	2.73	3.389(7)	131.6
N(2)−H(2C)···Cl(5)	0.89	2.96	3.717(2)	143.4
N(2)−H(2B)···Cl(4)#1	0.89	2.55	3.393(8)	157.6
N(2)−H(2B)···Cl(5)#1	0.89	2.91	3.384(8)	114.6
N(1)−H(1B)···Cl(6)#1	0.89	2.35	3.150(9)	149.0
N(1)−H(1C)···Cl(6)#2	0.89	2.48	3.223(8)	141.4
N(2)−H(2A)···Cl(6)#3	0.89	2.58	3.389(7)	152.3
N(1)−H(1A)···Cl(6)#4	0.89	2.79	3.584(9)	149.7
N(3)−H(3A)···Cl(3)#5	0.89	2.54	3.374(6)	155.4
N(3)−H(3B)···Cl(2)#6	0.89	2.57	3.288(7)	138.6
N(3)−H(3C)···Cl(1)#7	0.89	2.84	3.707(1)	164.1
N(4)−H(4A)···Cl(3)#8	0.89	2.88	3.602(10)	138.9
N(4)−H(4B)···Cl(3)#9	0.89	2.37	3.145(9)	146.3
N(4)−H(4C)···Cl(3)#2	0.89	2.38	3.122(9)	141.5
symmetry code: #1 $-x + 1, -y + 1, -z + 1$; #2 $x + 1, y, z$; #3 $x, -y + 3/2, z$; #4 $x + 1, -y + 1/2, z$; #5 $x, -y + 1/2, z$; #6 $-x + 1, -y + 1, -z$; #7 $x, y + 1, z$; #8 $-x + 1, y + 1/2, -z$; #9 $-x + 1, -y, -z$				

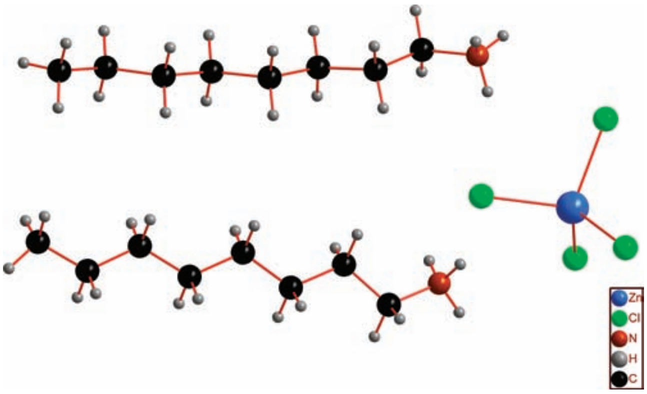


Figure 1. Molecular structure of $(1\text{-}C_8H_{17}NH_3)_2ZnCl_4(s)$.

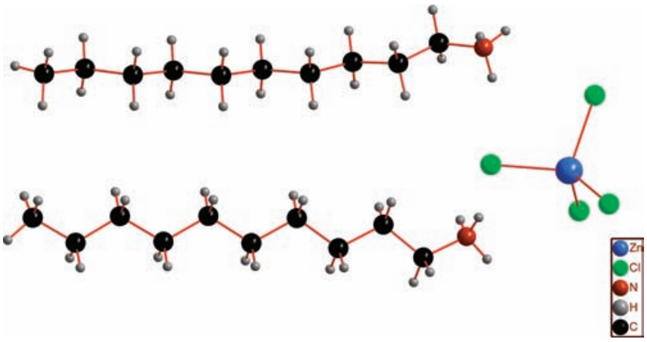


Figure 2. Molecular structure of $(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4(s)$.

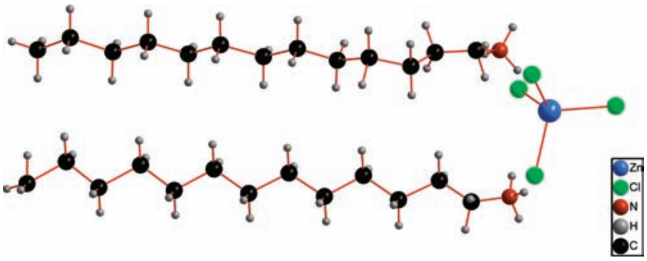


Figure 3. Molecular structure of $(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4(s)$.

these results of lattice potential energies (listed in Table 5) of the four compounds, it can be seen that lattice potential energies of $(1\text{-}C_8H_{17}NH_3)_2ZnCl_4$ (U_{POT} = 986.03 kJ·mol^{-1}), $(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4$ (U_{POT} = 931.45 kJ·mol^{-1}), $(1\text{-}C_{12}H_{25}NH_3)_2ZnCl_4$ (U_{POT} = 888.82 kJ·mol^{-1}), and $(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4$ (U_{POT} = 867.75 kJ·mol^{-1}) decrease with the volumes of cations in the following order: U_{POT} $[(1\text{-}C_8H_{17}NH_3)_2ZnCl_4]$ > U_{POT} $[(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4]$ > U_{POT} $[(1\text{-}C_{12}H_{25}NH_3)_2ZnCl_4]$ > U_{POT} $[(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4]$. The differences are caused mainly due to the different volumes of cations. The lattice potential energy is mainly dependent on electrostatic interaction, and the electrostatic interaction is inversely related to the volume of the ion. And in the case of $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, 12, and 13), the cation volume varies as follows: $V[1\text{-}C_{13}H_{27}NH_3]^+$ > $V[1\text{-}C_{12}H_{25}NH_3]^+$ > $V[1\text{-}C_{10}H_{21}NH_3]^+$ > $V[1\text{-}C_8H_{17}NH_3]^+$. So it is normal that lattice potential energies of $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, 12, and 13) decrease with the increase in the volumes of cations.

Ionic Volumes. For a salt of molecular formula M_pX_q, the molecular volume in accordance with the additive property of the volumes can be expressed as

$$V_m = pV_+ + qV_- \tag{4}$$

for the title compounds, V_+ is the volume of cation $[1\text{-}C_nH_{2n+1}NH_3]^+$, V_- is the volume of anion $[ZnCl_4]^{2-}$, p = 2, and q = 1. From eq 4, the volume of $[ZnCl_4]^{2-}$ can be calculated to be $V[ZnCl_4]^{2-}$ = 0.1406 nm^3 based on $V_m[(1\text{-}C_{12}H_{25}NH_3)_2ZnCl_4]$ = 0.8017 nm^3 and $V[1\text{-}C_{12}H_{25}NH_3]^+$ = 0.33056 nm^3.[19] And the volumes of $[1\text{-}C_8H_{17}NH_3]^+$, $[1\text{-}C_{10}H_{21}NH_3]^+$, and

$[1\text{-}C_{13}H_{27}NH_3]^+$ are calculated to be 0.2384, 0.2861, and 0.3553 nm^3, respectively. The results of the ionic volumes are listed in Table 5.

By comparison with the literature,[17] it can be seen that the $V[ZnCl_4]^{2-} = 0.1406$ nm^3 reported in this paper is smaller than the $V[ZnCl_4]^{2-} = (0.185 \pm 0.011)$ nm^3 in the literature. This is mainly because we have used a different volume of Cl^-. In 1999, Jenkins et al. calculated the volume of the $[ZnCl_4]^{2-}$ anion, $V[ZnCl_4]^{2-} = (0.185 \pm 0.011)$ nm^3, based on $V[Cl]^- = (0.047 \pm 0.013)$ nm^3. But in 2008, Glasser and Jenkins[20] corrected the original $V[Cl]^- = (0.047 \pm 0.013)$ nm^3 to be $V[Cl]^- = 0.0298$ nm^3, and we calculated the volume $V[1\text{-}C_{12}H_{25}NH_3]^+ = 0.33056$ nm^3 based on $V[Cl]^- = 0.0298$ nm^3 in 2009.[19] In this paper, we quote our previous work, and $V[ZnCl_4]^{2-}$ is calculated to be $V_- = 0.1406$ nm^3.

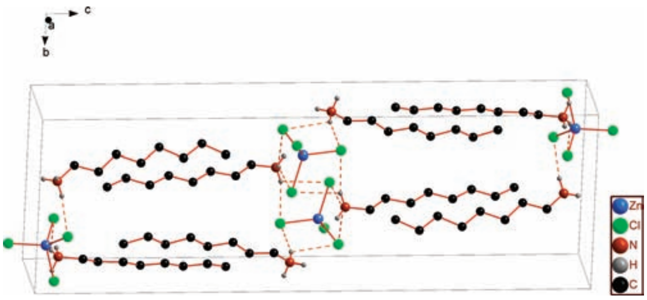


Figure 4. Packing diagram of $(1\text{-}C_8H_{17}NH_3)_2ZnCl_4(s)$.

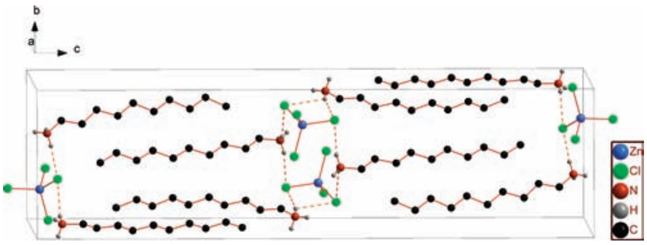


Figure 5. Packing diagram of $(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4(s)$.

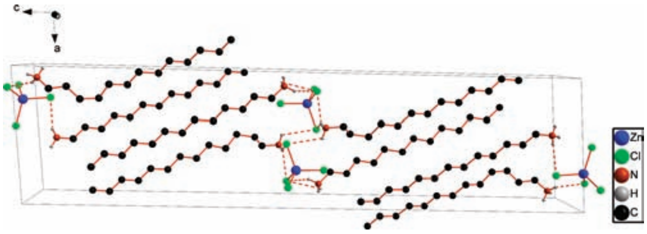


Figure 6. Packing diagram of $(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4(s)$.

Molar Enthalpies of Dissolution at Infinite Dilution and Sums of Pitzer's Parameters. $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, 12, and 13) can be dissolved in double-distilled water. The experimental values of molar enthalpies of dissolution ($\Delta_s H_m$) of the four title compounds in the double-distilled water are given in Table 6, and the curvilinear relationships of $\Delta_s H_m/(\text{kJ}\cdot\text{mol}^{-1})$ with molalities m ($\text{mol}\cdot\text{kg}^{-1}$) are shown in Figures 7−10.

The cryoscopic method has been used to determine the number of ions in the solutions. The experiments demonstrate that the molality of ions Σm_B in the solutions after the four title compounds are dissolved in water equals $7m$ (m is the molality of the solute) according to the ratio of the experimental values of freezing point depression to theoretical values. It is shown that these compounds are completely dissociated to $\{2[1\text{-}C_nH_{2n+1}NH_3]^+(aq) + Zn^{2+}(aq) + 4Cl^-(aq)\}$ in water. So, the dissolution process of $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, 12, and 13) may be expressed as

$$(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s) + WH_2O(l) \rightarrow 2[1-C_nH_{2n+1}NH_3]^+(aq) + Zn^{2+}(aq) + 4Cl^-(aq) \quad (5)$$

where W is the number of kilograms of solvent. G^{ex} can be expressed by Pitzer's unsymmetrical mixing electrolyte solution theory.

The general form of the excess Gibbs energy of electrolytes[8] is given by

$$G^{ex}/(WRT) = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) + \sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk} \quad (6)$$

in which $\lambda_{ij}(I)$ is the second virial coefficient for pairwise interaction between ions i and j, and it is a function of I. The ionic strength dependence may be neglected for the third virial coefficient μ_{ijk}, which represents the triple ion interactions and is important only at high concentrations. R is the molar gas constant, 8.3145 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. W is the number of kilograms of solvent, and $f(I)$ is a general function of the ionic strength I, which is related to the electrical forces. The expression selected for $f(I)$ is given by[8]

$$f(I) = -A_\phi(4I/b)\ln(1 + bI^{1/2}) \quad (7)$$

$$A_\phi = (1/3)(2\pi N_0 d_w/1000)^{1/2}(e^2/4\pi\varepsilon_0 DkT)^{3/2} \quad (8)$$

where b is a parameter with the value 1.2 $\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$ for all solutions and A_ϕ is the Debye−Hückel coefficient for the osmotic coefficient. D is the dielectric constant or relative permittivity, d_w is the density of the water or other solvent, e is the electronic

Table 5. Lattice Potential Energies and Ionic Volumes of $[1\text{-}C_nH_{2n+1}NH_3]^+$ (n = 8, 10, and 13)^a

compound	$U_{POT}/(\text{kJ}\cdot\text{mol}^{-1})$	V_m/nm^3	$V[ZnCl_4]^{2-}/\text{nm}^3$	$V[1\text{-}C_nH_{2n+1}NH_3]^+/\text{nm}^3$
$(1\text{-}C_8H_{17}NH_3)_2ZnCl_4$	986.03	0.6173	0.1406	0.2384
$(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4$	931.45	0.7129		0.2861
$(1\text{-}C_{12}H_{25}NH_3)_2ZnCl_4$	888.82	0.8017		0.3306
$(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4$	867.75	0.8511		0.3553

[a] U_{POT} is the lattice potential energy; V_m, the molecular volume; $V[ZnCl_4]^{2-}$, the volume of the anion $[ZnCl_4]^{2-}$; $V[1\text{-}C_nH_{2n+1}NH_3]^+$, the volume of the cation $[1\text{-}C_nH_{2n+1}NH_3]^+$.

Table 6. Values of Molar Enthalpies of Dissolution of the Title Compounds at Various Molalities at T = 298.15 K[a]

10^3m $(\text{mol}\cdot\text{kg}^{-1})$	Δ_sH_m $(\text{kJ}\cdot\text{mol}^{-1})$	$-2m$ $(\text{mol}\cdot\text{kg}^{-1})$	$-4my'$ $(\text{mol}\cdot\text{kg}^{-1})$	Y/K^{-1}
		$(1\text{-}C_8H_{17}NH_3)_2ZnCl_4(s)$		
0.223	16.52	−0.000447	−0.000855	0.0110
0.435	15.80	−0.000870	−0.00164	0.0104
0.643	15.17	−0.00129	−0.00239	0.00990
0.870	14.51	−0.00174	−0.00319	0.00939
1.078	14.02	−0.00216	−0.00391	0.00901
1.292	13.66	−0.00258	−0.00464	0.00872
1.494	13.48	−0.00299	−0.00533	0.00857
1.720	13.40	−0.00344	−0.00608	0.00847
1.934	13.35	−0.00387	−0.00679	0.00841
2.138	13.34	−0.00428	−0.00746	0.00837
2.559	13.32	−0.00512	−0.00881	0.00830
2.794	13.29	−0.00559	−0.00956	0.00825
3.218	13.27	−0.00644	−0.0109	0.00819
3.634	13.27	−0.00727	−0.0122	0.00814
4.064	13.25	−0.00813	−0.0135	0.00808
		$(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4(s)$		
0.201	38.68	−0.000402	−0.000771	0.0260
0.383	35.52	−0.000766	−0.00145	0.0237
0.575	34.05	−0.00115	−0.00214	0.0227
0.768	33.67	−0.00154	−0.00283	0.0224
0.959	33.53	−0.00192	−0.00350	0.0222
1.160	33.51	−0.00232	−0.00419	0.0222
1.340	33.51	−0.00268	−0.00481	0.0221
1.540	33.51	−0.00308	−0.00548	0.0221
1.760	33.55	−0.00352	−0.00622	0.0221
1.910	33.55	−0.00382	−0.00671	0.0221
2.110	33.56	−0.00422	−0.00737	0.0221
2.490	33.59	−0.00498	−0.00860	0.0220
2.870	33.62	−0.00574	−0.00980	0.0220
3.250	33.64	−0.00650	−0.0110	0.0220
3.630	33.62	−0.00726	−0.0122	0.0219
		$(1\text{-}C_{12}H_{25}NH_3)_2ZnCl_4(s)$		
0.163	55.87	−0.000329	−0.000629	0.0376
0.355	54.27	−0.000711	−0.00134	0.0364
0.532	53.18	−0.00106	−0.00199	0.0356
0.698	52.44	−0.00140	−0.00258	0.0351
0.872	51.75	−0.00174	−0.00320	0.0346
1.044	51.12	−0.00209	−0.00379	0.0341
1.215	50.60	−0.00243	−0.00438	0.0337
1.387	50.23	−0.00277	−0.00497	0.0335
1.554	50.02	−0.00311	−0.00553	0.0333
1.735	49.96	−0.00347	−0.00614	0.0332
1.900	49.92	−0.00380	−0.00668	0.0332
2.240	49.94	−0.00448	−0.00779	0.0331
2.592	49.95	−0.00519	−0.00892	0.0331
2.946	49.98	−0.00589	−0.0100	0.0331
3.461	50.03	−0.00692	−0.0116	0.0330
		$(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4(s)$		
0.171	63.00	−0.000342	−0.000658	0.0424
0.252	62.23	−0.000504	−0.000961	0.0419
0.337	61.58	−0.000674	−0.00128	0.0414
0.419	60.95	−0.000837	−0.00158	0.0409
0.494	60.51	−0.000988	−0.00185	0.0406
0.580	60.19	−0.00116	−0.00216	0.0404
0.663	59.98	−0.00133	−0.00246	0.0402
0.831	59.79	−0.00166	−0.00305	0.0400
0.993	59.75	−0.00199	−0.00362	0.0400
1.154	59.68	−0.00231	−0.00417	0.0399
1.320	59.64	−0.00264	−0.00474	0.0398
1.478	59.65	−0.00296	−0.00528	0.0398
1.653	59.61	−0.00331	−0.00586	0.0398
1.809	59.61	−0.00362	−0.00638	0.0397
1.974	59.60	−0.00395	−0.00692	0.0397

[a] m is the molality of the solute; Δ_sH_m is the molar enthalpy of dissolution of the compound; $y' = [1 - (1 + 2I^{1/2})\exp(-2I^{1/2})]/2I$; Y is the extrapolation function.

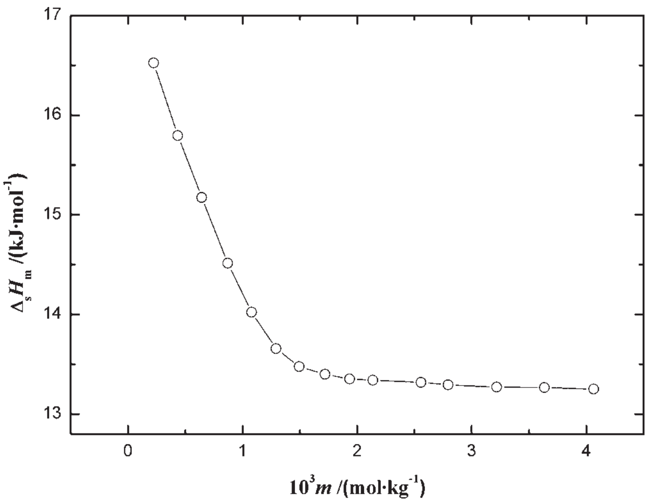


Figure 7. Plot of measured dissolution enthalpy of $(1\text{-}C_8H_{17}NH_3)_2ZnCl_4(s)$ as a function of molality.

charge, ε_0 is the permittivity of free space, N_0 is the Avogadro constant, and k is the Boltzmann constant.

The virial coefficients depend on the short-range forces between solute particles. The individual coefficients for ions cannot be measured. Therefore, measurable coefficients of electrically neutral combinations are defined by

$$B_{ca} = \lambda_{ca} + |z_a/2z_c|\lambda_{cc} + |z_c/2z_a|\lambda_{aa} \tag{9}$$

$$\theta_{cc'} = \lambda_{cc'} - (z_{c'}/2z_c)\lambda_{cc} - (z_c/2z_{c'})\lambda_{c'c'} \tag{10}$$

in which c and c′ are ions of the same sign and a is an ion of the opposite sign. The B terms can best be evaluated from the pure electrolyte data; the θ terms arise only for mixtures and can be evaluated from the common-ion mixtures.[9] Since λ depends on the ionic strength, so do B and θ. The following empirical expressions[10] have been found to represent satisfactorily the

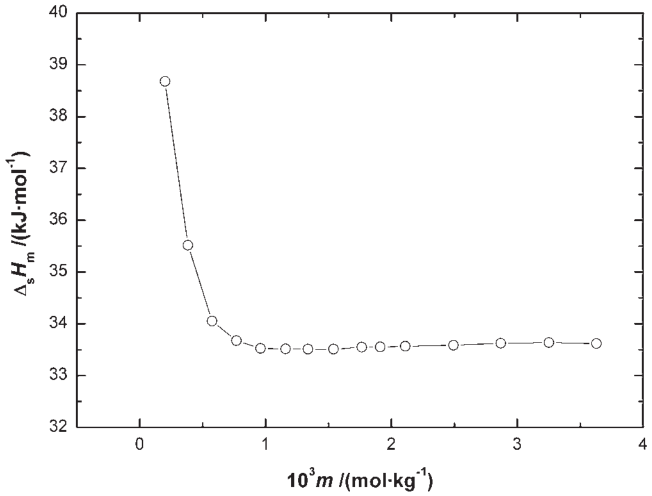


Figure 8. Plot of measured dissolution enthalpy of $(1\text{-}C_{10}H_{21}NH_3)_2$-$ZnCl_4(s)$ as a function of molality.

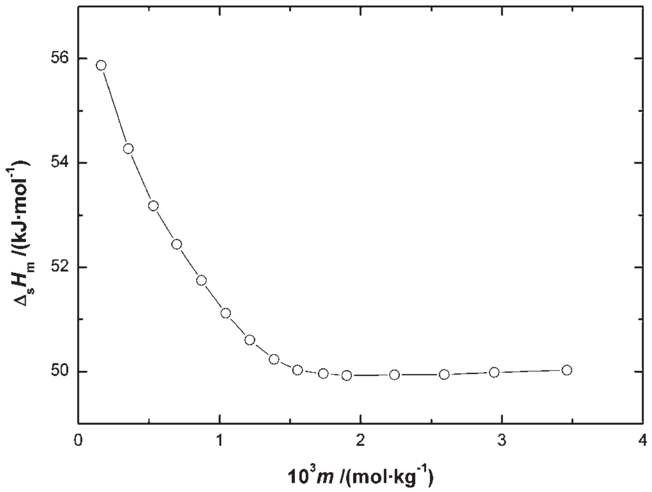


Figure 9. Plot of measured dissolution enthalpy of $(1\text{-}C_{12}H_{25}NH_3)_2$-$ZnCl_4(s)$ as a function of molality.

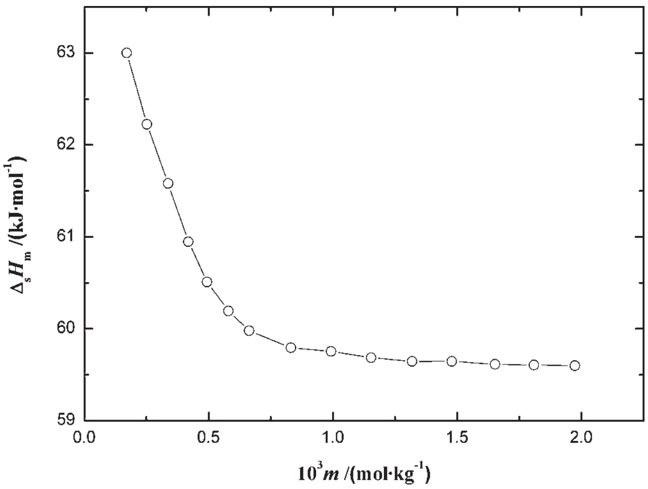


Figure 10. Plot of measured dissolution enthalpy of $(1\text{-}C_{13}H_{27}NH_3)_2$-$ZnCl_4(s)$ as a function of molality.

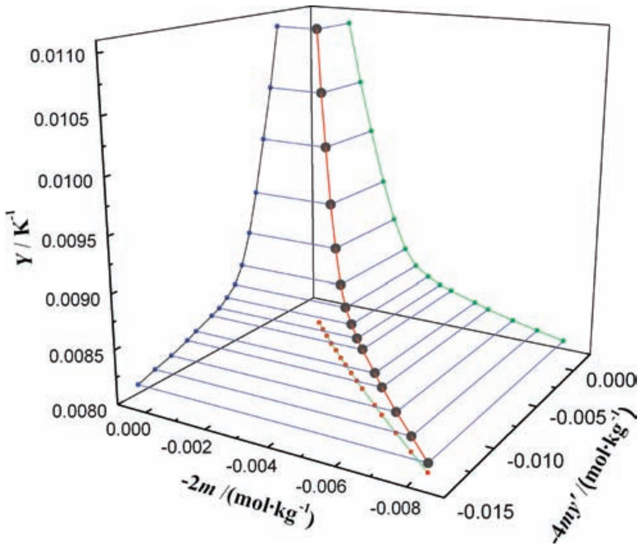


Figure 11. The 3D chart of Y against $-2m$ and $-4my'$ for $(1\text{-}C_8H_{17}$-$NH_3)_2ZnCl_4(s)$.

ionic strength dependence of B and θ:

$$B_{ca} = \beta^{(0)}_{ca} + (2\beta^{(1)}_{ca}/\alpha^2 I)[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})] \tag{11}$$

$$\theta_{cc'} = \theta^{(0)}_{cc'} + (2\theta^{(1)}_{cc'}/\alpha^2 I)[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})] \tag{12}$$

where the value of α is normally equal to 2.0 kg$^{1/2}\cdot$mol$^{-1/2}$, and $\beta^{(0)}_{ca}$, $\beta^{(1)}_{ca}$, $\theta^{(0)}_{ca}$, and $\theta^{(1)}_{ca}$ are characteristic parameters of the electrolyte. We substitute eqs 9–12 into eq 6 and obtain[8]

$$G^{ex}/(WRT) = f(I) + 2\sum_{c}\sum_{a} m_c m_a B_{ca} + 2\sum_{c}\sum_{c'} m_c m_{c'} \theta_{cc'} \tag{13}$$

Since the electrolyte solution of each title compound may be regarded as a unsymmetrical mixed electrolyte solution, $2(1\text{-}C_nH_{2n+1}NH_3Cl)-ZnCl_2$ and $m_{[1\text{-}C_nH_{2n+1}NH_3]^+} = 2m$, $m_{Zn^{2+}} = m$, and $m_{Cl^-} = 4m$, eq 13 can be rewritten as follows:

$$\begin{aligned} G^{ex}/WRT = {} & -(4A_{\phi}I/b)\ln(1 + bI^{1/2}) \\ & + 4m^2(4\beta^{(0)}_{1\text{-}C_nH_{2n+1}NH_3,\,Cl} + 2\beta^{(0)}_{Zn,\,Cl} + \theta_{1\text{-}C_nH_{2n+1}NH_3,\,Zn}) \\ & + 8m^2(2\beta^{(1)}_{1\text{-}C_nH_{2n+1}NH_3,\,Cl} + \beta^{(1)}_{Zn,\,Cl})y' \end{aligned} \tag{14}$$

where $y' = [1 - (1 + 2I^{1/2})\exp(-2I^{1/2})]/2I$. The equation for the excess enthalpy $L = H^{ex}$ following from the temperature differentiation[9] of eq 14 can be expressed as

$$\begin{aligned} L = {} & (WRT^2)[(A_H I/bRT^2)\ln(1 + bI^{1/2}) \\ & - 4m^2(4\beta^{(0)L}_{1\text{-}C_nH_{2n+1}NH_3,\,Cl} + 2\beta^{(0)L}_{Zn,\,Cl} + \theta^{L}_{1\text{-}C_nH_{2n+1}NH_3,\,Zn}) \\ & - 8m^2(2\beta^{(1)L}_{1\text{-}C_nH_{2n+1}NH_3,\,Cl} + \beta^{(1)L}_{Zn,\,Cl})y'] \end{aligned} \tag{15}$$

$$\beta^{(0)L}_{ca} = (\partial\beta^{(0)}_{ca}/\partial T)_P \tag{16}$$

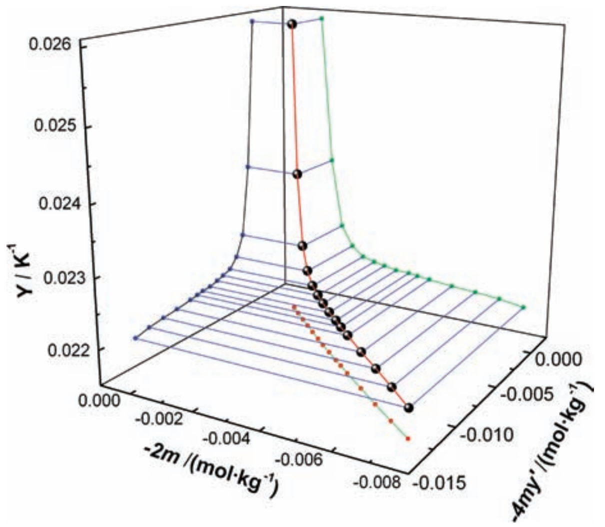


Figure 12. The 3D chart of Y against $-2m$ and $-4my'$ for (1-$C_{10}H_{21}$-$NH_3)_2ZnCl_4$(s).

$$\beta_{\text{ca}}^{(1)L} = (\partial \beta_{\text{ca}}^{(1)}/\partial T)_p \tag{17}$$

$$\theta_{\text{cc}'}^{L} = (\partial \theta_{\text{cc}'}/\partial T)_p \tag{18}$$

$$A_H = 4RT^2(\partial A_\phi/\partial T)_p \tag{19}$$

where A_H is the Debye–Hückel parameter for enthalpy,[10] A_H = 1986 J·mol^{-1} at T = 298.15 K.

From the above equations and the excess enthalpy $L = H^{\text{ex}}$, a working equation to determine the Pitzer parameter is shown as

$$\begin{aligned} Y &= \Delta_s H_m/2RT^2 - (1/2m)(A_H I/1.2RT^2)\ln(1 + 1.2I^{1/2}) \\ &= \alpha_0 - 2m(4\beta^{(0)L}_{1\text{-}C_nH_{2n+1}NH_3,\,Cl} + 2\beta^{(0)L}_{Zn,\,Cl} + \theta^{L}_{1\text{-}C_nH_{2n+1}NH_3,\,Zn}) \\ &\quad - 4my'(2\beta^{(1)L}_{1\text{-}C_nH_{2n+1}NH_3,\,Cl} + \beta^{(1)L}_{Zn,\,Cl}) \end{aligned} \tag{20}$$

where Y is the extrapolation function and $\alpha_0 = \Delta_s H_m^\infty/(2RT^2)$. The values of Y, $-2m$, and $-4my'$ are given in Table 6. The 3D chart of Y against $-2m$ and $-4my'$ is plotted in Figures 11–14.

Regression of Y against $-2m$ and $-4my'$ is made by least-squares to obtain α_0, $(4\beta^{(0)L}_{1\text{-}C_nH_{2n+1}NH_3,Cl} + 2\beta^{(0)L}_{Zn,Cl} + \theta_{1\text{-}C_nH_{2n+1}NH_3,Zn}{}^L)$, $(2\beta^{(1)L}_{1\text{-}C_nH_{2n+1}NH_3,Cl} + \beta^{(1)L}_{Zn,Cl})$, and the standard deviation of fitting. And molar enthalpies of dissolution of (1-$C_nH_{2n+1}NH_3)_2ZnCl_4$(s) (n = 8, 10, 12, and 13) at infinite dilution are determined using $\alpha_0 = \Delta_s H_m^\infty/(2RT^2)$. The values of α_0, $(4\beta^{(0)L}_{1\text{-}C_nH_{2n+1}NH_3,Cl} + 2\beta^{(0)L}_{Zn,Cl} + \theta^{L}_{1\text{-}C_nH_{2n+1}NH_3,Zn})$, $(2\beta^{(1)L}_{1\text{-}C_nH_{2n+1}NH_3,Cl} + \beta^{(1)L}_{Zn,Cl})$, $\Delta_s H_m^\infty$, and standard deviations for each compound are given in Table 7 .

Since lattice potential energies of the title compounds vary as U_{POT} [(1-$C_8H_{17}NH_3)_2ZnCl_4$] > U_{POT} [(1-$C_{10}H_{21}NH_3)_2$-$ZnCl_4$] > U_{POT} [(1-$C_{12}H_{25}NH_3)_2ZnCl_4$] > U_{POT} [(1-$C_{13}H_{27}$-$NH_3)_2ZnCl_4$], it can be presumed that the heat absorbed when compounds are dissolved in the water should increase along with lattice potential energies. However, in this paper, the results indicate that molar enthalpies of dissolution of four compounds at infinite dilution vary as $\Delta_s H_m^\infty$[(1-$C_8H_{17}NH_3)_2ZnCl_4$] < $\Delta_s H_m^\infty$[(1-$C_{10}H_{21}NH_3)_2ZnCl_4$] < $\Delta_s H_m^\infty$[(1-$C_{12}H_{25}NH_3)_2$-$ZnCl_4$] < $\Delta_s H_m^\infty$[(1-$C_{13}H_{27}NH_3)_2ZnCl_4$]. It is mainly ascribed to the thermal effect of the cation proportionally with the ratio of the charge to the volume, and the differences between lattice potential energies of the four compounds are compensated by thermal effects of the cations in generating hydrated cations when the compounds are dissolved in the water.

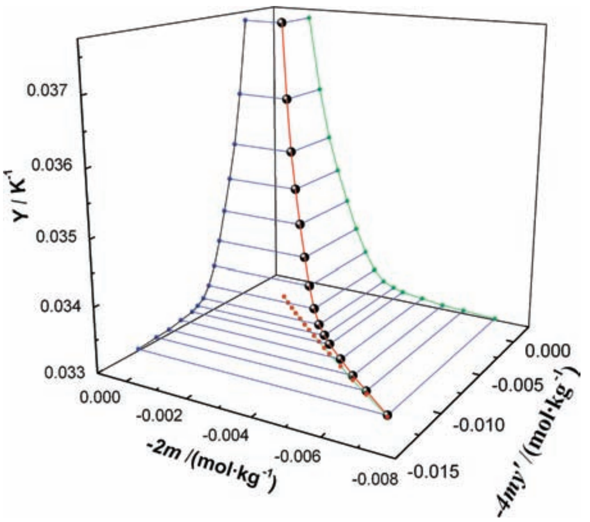


Figure 13. The 3D chart of Y against $-2m$ and $-4my'$ for (1-$C_{12}H_{25}$-$NH_3)_2ZnCl_4$(s).

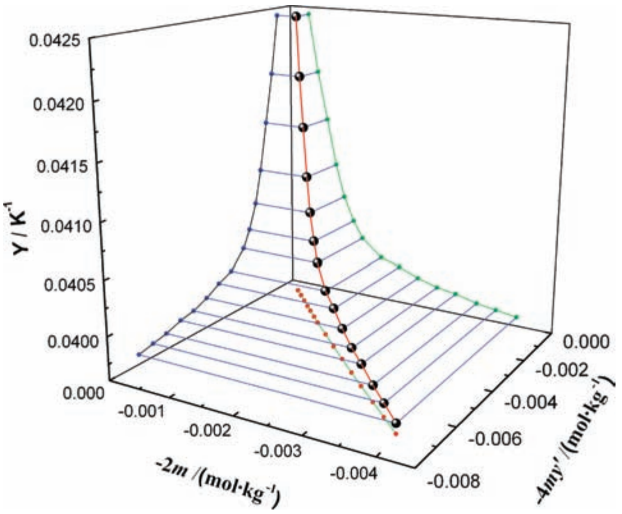


Figure 14. The 3D chart of Y against $-2m$ and $-4my'$ for (1-$C_{13}H_{27}$-$NH_3)_2ZnCl_4$(s).

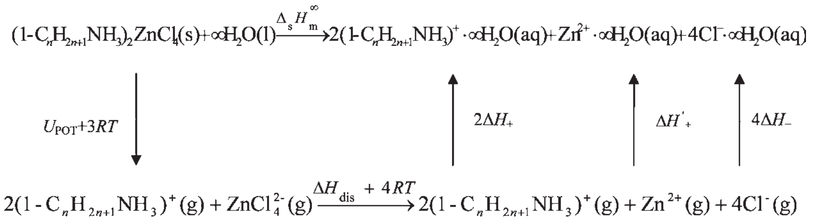
From the values of molar enthalpies of dissolution, we deduce that the dissolution of each title compound in the water is a typical endothermic process, which indicates that it should be an entropy-driven process instead of an enthalpy-driven process. As is known, the group $-C_nH_{2n+1}$ is a hydrophobic alkyl group, which can reduce the solubility of the title compounds in the water. And a certain amount of heat is required when the ionic bonds and hydrogen bonds are broken. In addition, hydration of the ion needs to give off some heat quantity. So, on the one hand, the existence of hydrophobic alkyl groups ($-C_nH_{2n+1}$) in each compound leads to the weakening of the hydration effect of the cation when met with the solvent, and the hydration heat is reduced by comparison with some normal or inorganic cations. On the other hand, the breaking of ionic bonds and

Table 7. Results of Fitting for the Four Compounds[a]

compound	α_0	$(4\beta^{(0)L}_{1\text{-}C_nH_{2n+1}NH_3,Cl} + 2\beta^{(0)L}_{Zn,Cl} + \theta^{L}_{1\text{-}C_nH_{2n+1}NH_3,Zn})$	$(2\beta^{(1)L}_{1\text{-}C_nH_{2n+1}NH_3,Cl} + \beta^{(1)L}_{Zn,Cl})$	$10^4 s$	$\Delta_s H_m^\infty$ (kJ·mol^{-1})
$(1\text{-}C_8H_{17}NH_3)_2ZnCl_4$	0.01142 ± 0.00015	−6.473	4.135	1.653	16.880 ± 0.228
$(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4$	0.02539 ± 0.00055	−10.560	6.552	5.883	37.529 ± 0.808
$(1\text{-}C_{12}H_{25}NH_3)_2ZnCl_4$	0.03823 ± 0.00023	−14.144	8.829	2.116	56.509 ± 0.336
$(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4$	0.04310 ± 0.00023	−20.852	12.344	2.114	63.707 ± 0.333

[a] $\Delta_s H_m^\infty$ is the molar enthalpy of dissolution of the compound at infinite dilution; $(4\beta^{(0)L}_{1\text{-}C_nH_{2n+1}NH_3,Cl} + 2\beta^{(0)L}_{Zn,Cl} + \theta^{L}_{1\text{-}C_nH_{2n+1}NH_3,Zn})$ and $(2\beta^{(1)L}_{1\text{-}C_nH_{2n+1}NH_3,Cl} + \beta^{(1)L}_{Zn,Cl})$ are the sums of Pitzer's parameters; s is fitting standard deviation; $\alpha_0 = \Delta_s H_m^\infty/(2RT^2)$.

Scheme 1. Thermodynamic Cycle for Calculating the Dissociation Enthalpy of $[ZnCl_4]^{2-}$(g) and the Hydration Enthalpy of $[1\text{-}C_nH_{2n+1}NH_3]^+$



hydrogen bonds existing in each compound needs to absorb additional heat. Therefore, the endothermic process takes place because the heat quantity given off from the hydration of each compound is smaller than that absorbed due to the breaking of ionic bonds and hydrogen bonds in each solid compound.[9]

Dissociation Enthalpy of $[ZnCl_4]^{2-}$ and Hydration Enthalpies of the Cations. The thermodynamic cycle used to calculate the dissociation enthalpy of $[ZnCl_4]^{2-}$(g) and hydration enthalpy of $[1\text{-}C_nH_{2n+1}NH_3]^+$ is indicated in Scheme 1.

In Scheme 1, the thermal effects to generate $[1\text{-}C_nH_{2n+1}NH_3]^+\cdot\infty H_2O(aq)$, $Zn^{2+}\cdot\infty H_2O$ (aq), and $Cl^- \cdot \infty H_2O(aq)$ from $[1\text{-}C_nH_{2n+1}NH_3]^+(g)$, $Zn^{2+}(g)$, and $Cl^-(g)$ are the sum of hydration enthalpies of corresponding ions. Thus, the calculation formula of dissociation enthalpy (ΔH_{dis}) can be deduced according to the thermodynamic cycle:

$$\Delta_s H_m^\infty = (U_{POT} + 3RT) + (\Delta H_{dis} + 4RT) + (2\Delta H_+ + \Delta H'_+ + 4\Delta H_-) \quad (21)$$

in which ΔH_+ is the hydration enthalpy of $[1\text{-}C_nH_{2n+1}NH_3]^+(g)$, $\Delta H'_+$ is the hydration enthalpy of $Zn^{2+}(g)$, and ΔH_- is that of $Cl^-(g)$. Therefore, the dissociation enthalpy of $[ZnCl_4]^{2-}(g)$ can be calculated as $\Delta H_{dis} = (2741.31 \pm 0.81)$ kJ·mol^{-1} from eq 21 on the basis of lattice potential energy ($U_{POT} = 931.45$ kJ·mol^{-1}), molar enthalpy of dissolution at infinite dilution ($\Delta_s H_m^\infty = (37.529 \pm 0.808)$ kJ·mol^{-1}), and hydration enthalpies of ions[21,22] ($\Delta H_+ = -57.29$ kJ·mol^{-1}, $\Delta H'_+ = -2070$ kJ·mol^{-1} and $\Delta H_- = -367$ kJ·mol^{-1}) of $(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4$. Hydration enthalpies of the cations of the rest of the title compounds can be calculated to be $\Delta H_+[1\text{-}C_8H_{17}NH_3]^+ = -(94.90 \pm 0.42)$ kJ·mol^{-1}, $\Delta H_+[1\text{-}C_{12}H_{25}NH_3]^+ = -(26.48 \pm 0.44)$ kJ·mol^{-1}, and $\Delta H_+[1\text{-}C_{13}H_{27}NH_3]^+ = -(12.35 \pm 0.44)$ kJ·mol^{-1} on the basis of the dissociation enthalpy of $[ZnCl_4]^{2-}(g)$. These results indicate that a strong endothermic reaction takes place when $[ZnCl_4]^{2-}(g)$ is dissociated to $Zn^{2+}(g)$ and $Cl^-(g)$, and it is not a very strong endothermic reaction when $[1\text{-}C_nH_{2n+1}NH_3]^+$(g) ($n$ = 8, 10, 12, and 13) are dissociated in double-distilled water. The absolute values of hydration enthalpies of the cations decrease with the volumes of the cations in the order $\Delta H_+[1\text{-}C_8H_{17}NH_3]^+ > \Delta H_+[1\text{-}C_{10}H_{21}NH_3]^+ > \Delta H_+[1\text{-}C_{12}H_{25}NH_3]^+ > \Delta H_+[1\text{-}C_{13}H_{27}NH_3]^+$. It is caused mainly by the hydration enthalpy being inversely related to the volume of the hydrophobic alkyl group when a compound is dissolved in the water.

CONCLUSIONS

All four compounds are crystallized in the monoclinic form with $Z = 4$, and their unit cell dimensions are very close.

The lattice potential energies and ionic volumes of the four compounds are obtained from crystallographic data. And lattice potential energies decrease with the increase of the volumes of cations. It is mainly ascribed to electrostatic interaction being inversely related to the volume of the ion.

The molar enthalpies of dissolution of the title compounds at infinite dilution are determined by application of the Pitzer model. And these values increase along with the volumes of cations. That is mainly due to the thermal effect of the cation proportionally with the ratio of the charge to the volume.

The endothermic reactions take place when $(1\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4(s)$ (n = 8, 10, 12, and 13) are dissolved in the double-distilled water because the hydration enthalpies of all of $2(1\text{-}C_nH_{2n+1}NH_3)^+(g)$, $Zn^{2+}(g)$, and $4Cl^-(g)$ are offset by the large dissociation enthalpy of $[ZnCl_4]^{2-}(g)$ and lattice potential energies of the title compounds.

ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic files in CIF format for the compounds $(1\text{-}C_8H_{17}NH_3)_2ZnCl_4$, $(1\text{-}C_{10}H_{21}NH_3)_2ZnCl_4$, and $(1\text{-}C_{13}H_{27}NH_3)_2ZnCl_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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