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Crystal structure and thermochemical properties of bis(1-octylammonium) tetrachlorocuprate

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Abstract Bis(1-octylammonium) tetrachlorocuprate (1-$C_8H_{17}NH_3)_2CuCl_4$(s) was synthesized by the method of liquid phase reaction. The crystal structure of the compound has been determined by X-ray crystallography. The lattice potential energy was obtained from the crystallographic data. Molar enthalpies of dissolution of (1-$C_8H_{17}NH_3)_2CuCl_4$(s) at various molalities were measured at 298.15 K in the double-distilled water by means of an isoperibol solution-reaction calorimeter, respectively. In terms of Pitzer's electrolyte solution theory, the molar enthalpy of dissolution of (1-$C_8H_{17}NH_3)_2CuCl_4$(s) at infinite dilution was determined to be $\Delta_s H_m^{\infty} = -5.972\,\mathrm{kJ\ mol^{-1}}$, and the sums of Pitzer's parameters $(4\beta^{(0)L}_{C_8H_{17}NH_3,Cl} + 2\beta^{(0)L}_{Cu,Cl} + \theta^{L}_{C_8H_{17}NH_3,Cu})$ and $(2\beta^{(1)L}_{C_8H_{17}NH_3,Cl} + \beta^{(1)L}_{Cu,Cl})$ were obtained.

Keywords Bis(1-octylammonium) tetrachlorocuprate · Lattice potential energy · Standard molar enthalpy of dissolution · Pitzer's theory

Introduction

A series of bis(1-alkylammonium) tetrachlorocuprate (II) (1-$C_nH_{2n+1}NH_3)_2CuCl_4$ (C_nCu, where $n = 8$–18) are an advanced solid–solid phase change materials (SSPCMs) [1, 2]. In the past decades, these compounds have been extensively investigated since they show many advantages over the solid–liquid phase change materials such as small change in volume, no volatilization, low temperature and high enthalpy of solid–solid phase transition [3, 4]. Those researches are focused on phase transitions of (1-$C_{12}H_{25}NH_3)_2CuCl_4$, (1-$C_{14}H_{29}NH_3)_2CuCl_4$, and (1-$C_{16}H_{33}NH_3)_2CuCl_4$. However, the crystal structure, lattice potential energy, and some basic thermochemical data of (1-$C_8H_{17}NH_3)_2CuCl_4$ have not been reported until now, which are needed to develop its new application fields and to carry out relevant theoretical research. For the purpose of the application and theoretical research concerned with the title compound, in this study, (1-$C_8H_{17}NH_3)_2CuCl_4$ is synthesized and the crystal structure is determined by X-ray crystallography, lattice potential energy is calculated from the crystallographic data, and the molar enthalpies of dissolution are determined by means of an isoperibol solution-reaction calorimeter.

Solution-reaction calorimetry is one of the classical methods to obtain the standard molar enthalpy of dissolution at infinite dilution and the dissociation enthalpy of coordination ion of many organic and inorganic compounds, especially useful for the determination of liquid–liquid and liquid–solid systems. In this study, the molar enthalpies of dissolution of (1-$C_8H_{20}NH_3)_2CuCl_4$(s) at different concentrations are determined by an isoperibol solution-reaction calorimeter. According to Pitzer's electrolyte solution theory, the molar enthalpy of dissolution of (1-$C_8H_{17}NH_3)_2CuCl_4$(s) at infinite dilution is determined, the sums of Pitzer's parameters $(4\beta^{(0)L}_{C_8H_{17}NH_3,Cl} + 2\beta^{(0)L}_{Cu,Cl} + \theta^{L}_{C_8H_{17}NH_3,Cu})$ and $(2\beta^{(1)L}_{C_8H_{17}NH_3,Cl} + \beta^{(1)L}_{Cu,Cl})$ are obtained.

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Experimental section

Synthesis of the title compound

Octylamine, hydrochloric acid (37 mass%), and copper chloride chosen as the reactants and anhydrous ethyl alcohol used as the solvent are all of analytical grade. The reactants are accurately weighed at the molar ratio of $n(C_8H_{17}NH_2)$:$n(HCl)$:$n(CuCl_2) = 2:2:1$ and slowly dissolved into anhydrous ethyl alcohol under sufficient stirring. The mixture is heated and stirred under refluxing for 6 h. After solution is boiled and refluxed for 6 h, the mixture is condensed by boiling off some of the liquid until crystal membrane emerges from the solution surface. The final solution is naturally cooled to room temperature, filtered, and golden yellow transparent crystal is obtained. The product is re-crystallized for three times with anhydrous ethyl alcohol and colorless crystal is gained. Finally, the sample is placed in a vacuum desiccator at $T = 303.15$ K to dry in vacuum for 12 h, the final product is placed in a weighing bottle and preserved in a desiccator. The mass fraction purity of the compound is determined by chemical and element analyses (model: PE-2400, Perkin Elmer, USA). The results show that practical contents of Cu, Cl, C, H, and N in the compound have been measured to be 13.68, 30.42, 41.22, 8.66, and 6.02%, respectively. Theoretical contents of Cu, Cl, C, H, and N in the compound have been calculated to be 13.64, 30.44, 41.25, 8.65, and 6.01%, respectively. This shows that the purity of the sample prepared is higher than 99.71 mol%.

Table 1 Crystal data and structure refinement for $(1\text{-}C_8H_{17}NH_3)_2CuCl_4(s)$

Empirical formula	$C_{16}H_{40}N_2CuCl_4$
Formula weight	465.84
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	$a = 7.3050(7)$ Å, $\alpha = 96.572(2)°$
	$b = 7.4721(8)$ Å, $\beta = 92.1140(10)°$
	$c = 22.785(2)$ Å, $\gamma = 90.2190(10)°$
Volume	1234.6(2) $Å^3$
Z, calculated density	2, 1.253 g cm^{-3}
Absorption coefficient	1.319 mm^{-1}
$F(000)$	494
Crystal size	0.45 × 0.38 × 0.11 mm^3
Theta range for data collection	1.80–25.01°
Limiting indices	$-8 \le h \le 6, -8 \le k \le 8, -21 \le l \le 27$
Reflections collected/unique	6560/4287 [R(int) = 0.0775]
Completeness to theta = 24.99	98.3%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8685 and 0.5884
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4287/343/215
Goodness-of-fit on F^2	0.963
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1218$, $wR_2 = 0.3106$
R indices (all data)	$R_1 = 0.1807$, $wR_2 = 0.3475$
Largest diff. peak and hole	1.447 and −1.048 e$Å^{-3}$

X-ray crystallography

A single crystal suitable for X-ray analysis is glued to a fine glass fiber and then mounted on the Bruker Smart-1000 CCD diffractometer with Mo-Kα radiation [5], $\lambda = 0.71073$ Å. The intensity data is collected at (298 ± 2) K. The structure is solved by direct methods and expanded using Fourier techniques with SHELXL-97 program [6]. The non-hydrogen atoms are refined anisotropically by full-matrix least-squares calculations on F^2 [7]. The hydrogen atoms are added theoretically, riding on the concerned atoms, and not refined. Crystallographic data for the structural analysis of $(1\text{-}C_8H_{17}NH_3)_2CuCl_4(s)$ has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 805760. Crystal data and refinement details are summarized in Table 1.

Isoperibol solution-reaction calorimetry

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 system. The principle and structure of the calorimeter are described in detail elsewhere [8].

The reliability of the calorimeter is verified previously by measuring dissolution enthalpy of KCl (calorimetrically primary standard) in the 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 double-distilled water at $T = (298.15 \pm 0.001)$ 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 [9]. This shows that the relative deviation between the literature value and the measuring value is within ±0.3%.

Results and discussion

Description of crystal structure

The crystal parameters, data collection, and refinement results for the compound are listed in Table 1. It is found from Table 1 that crystal system of the compound is triclinic, space group is *P*-1, unit cell dimensions are $a = 7.3050(7)$ Å, $b = 7.4721(8)$ Å, $c = 22.785(2)$ Å, $\alpha = 96.572(2)°$, $\beta = 92.1140(10)°$, $\gamma = 90.2190(10)°$, and $Z = 2$. The calculated density of the compound is 1.253 g cm^{-3} and the volume of formula unit is 1234.6(2) $Å^3$. Selected bond lengths and bond angles are listed in Table 2. The geometries of the hydrogen bonding are listed in Table 3. The molecular structure in crystallographic independent unit of $(1\text{-}C_8H_{17}NH_3)_2CuCl_4$ is shown in Fig. 1, and the packing of the cell structure is plotted in Fig. 2.

From Fig. 1 and Table 2, we can see that the steric configuration of $[CuCl_4]^{2-}$ in the coordination compound $(1\text{-}C_8H_{17}NH_3)_2CuCl_4$ is almost square. And there are two types of monomeric $[CuCl_4]^{2-}$ in the molecular structure, which may be caused by the unequal bond lengths (Cu–Cl) and the bond angles (Cl–Cu–Cl) in the crystallology aspect. But from the chemical composition, the two $[CuCl_4]^{2-}$ units are equal within experimental errors. The differences

Table 2 Selected bond lengths (Å) and bond angles (°) for $(1\text{-}C_8H_{17}NH_3)_2CuCl_4$

Cu(1)–Cl(12)	2.272(4)
Cu(1)–Cl(12)#1	2.272(4)
Cu(1)–Cl(9)#1	2.278(2)
Cu(1)–Cl(9)	2.278(2)
Cu(2)–Cl(6)	2.273(4)
Cu(2)–Cl(6)#2	2.273(4)
Cu(2)–Cl(5)#2	2.279(3)
Cu(2)–Cl(5)	2.279(3)
Cu(2)–Cl(9)	2.963(2)
Cl(12)–Cu(1)–Cl(12)#1	180.0
Cl(12)–Cu(1)–Cl(9)#1	89.94(12)
Cl(12)#1–Cu(1)–Cl(9)#1	90.06(12)
Cl(12)–Cu(1)–Cl(9)	90.06(12)
Cl(12)#1–Cu(1)–Cl(9)	89.94(12)
Cl(9)#1–Cu(1)–Cl(9)	180.00(9)
Cl(6)–Cu(2)–Cl(6)#2	180.00(4)
Cl(6)–Cu(2)–Cl(5)#2	90.09(12)
Cl(6)#2–Cu(2)–Cl(5)#2	89.91(12)
Cl(6)–Cu(2)–Cl(5)	89.91(12)
Cl(6)#2–Cu(2)–Cl(5)	90.09(12)
Cl(5)#2–Cu(2)–Cl(5)	180.0
Cl(6)–Cu(2)–Cl(9)	89.09(10)
Cl(6)#2–Cu(2)–Cl(9)	90.91(10)
Cl(5)#2–Cu(2)–Cl(9)	88.38(8)
Cl(5)–Cu(2)–Cl(9)	91.62(8)
Cu(1)–Cl(9)–Cu(2)	168.34(16)

Symmetry codes: #1 [$-x + 1, -y, -z$]; #2 [$-x + 2, -y + 1, -z$]

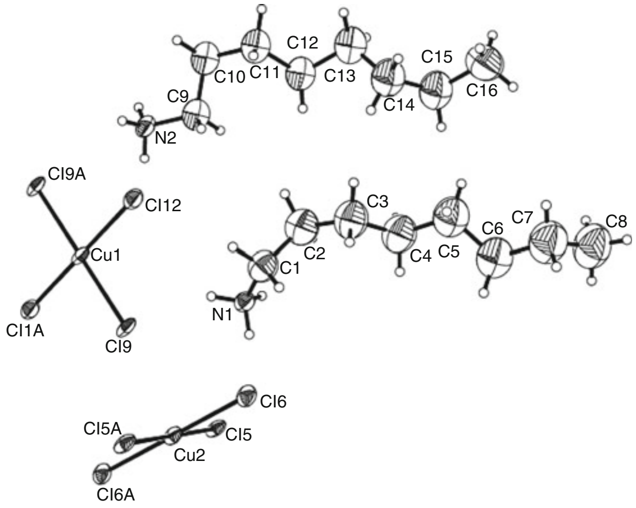

Fig. 1 Molecular structure in the crystallographic independent unit of $(1\text{-}C_8H_{17}NH_3)_2CuCl_4(s)$

Table 3 Hydrogen bond lengths (Å) and bond angles (°) for $(1\text{-}C_8H_{17}NH_3)_2CuCl_4$

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA
N(1)–H(1A)···Cl(5)#3	0.89	2.50	3.239(11)	141.2
N(1)–H(1C)···Cl(9)#3	0.89	2.90	3.437(11)	120.4
N(1)–H(1A)···Cl(9)	0.89	2.70	3.322(12)	127.9
N(1)–H(1B)···Cl(5)	0.89	2.64	3.390(11)	142.7
N(1)–H(1B)···Cl(6)	0.89	2.90	3.588(12)	135.1
N(1)–H(1C)···Cl(12)#4	0.89	2.81	3.306(12)	116.6
N(2)–H(2A)···Cl(6)#5	0.89	2.61	3.268(12)	131.8
N(2)–H(2C)···Cl(5)#5	0.89	2.85	3.408(12)	122.5
N(2)–H(2A)···Cl(9)#1	0.89	2.83	3.402(13)	123.0
N(2)–H(2B)···Cl(5)#3	0.89	2.49	3.344(12)	161.8
N(2)–H(2C)···Cl(12)#6	0.89	2.92	3.743(13)	155.1

Symmetry codes: #1 [$-x + 1, -y, -z$]; #3 [$-x + 1, -y + 1, -z$]; #4 [$x, y + 1, z$]; #5 [$x - 1, y - 1, z$]; #6 [$x - 1, y, z$]

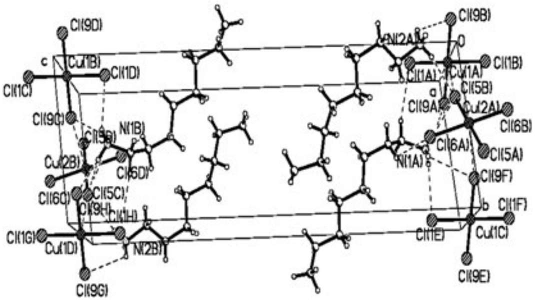

Fig. 2 Packing structure of the compound $(1\text{-}C_8H_{17}NH_3)_2CuCl_4(s)$

are probably mainly due to inaccuracy in the structure analysis and the different crystal forces for all chlorine atoms. As shown in Fig. 2, the hydrogen bonds N–H···Cl together with the van der Waals forces exist in the crystal to stabilize the structure. All hydrogen atoms are placed in geometrically idealized positions and constrained to ride on their parent atom (N).

Lattice potential energy of the compound

Equation 1 is used to estimate lattice potential energy for the general type of the salts of M_pX_q:

$$U_{\mathrm{POT}} = |z_+||z_-|v(\alpha'/V_{\mathrm{m}}^{1/3} + \beta'), \tag{1}$$

where z_+ and z_- are the respective charges on the cation and anion of the compound, v is the number of ions per molecule and equals $(p + q)$. For the case of salts of formula M_2X with charge ratio (1:2) such as $(1\text{-}C_8H_{17}NH_3)_2CuCl_4$, $z_+ = 1$, $z_- = 2$, $p = 2$, $q = 1$, $v = 3$, $\alpha' = 165.3$ kJ mol^{-1} nm, $\beta' = -29.8$ kJ mol^{-1}, and V_{m} is in units of nm^3 [10],

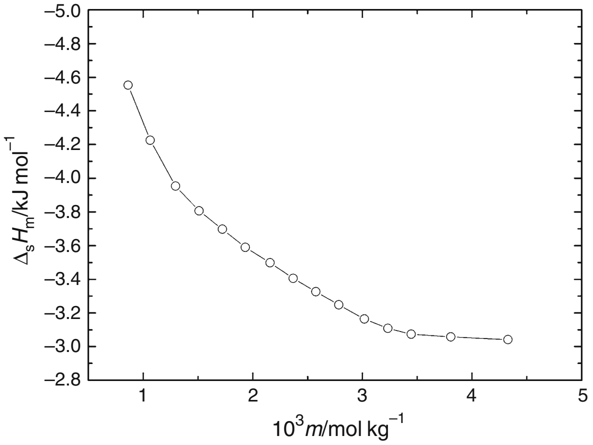

Fig. 3 Plot of measured dissolution enthalpy $\Delta_s H_m$ of $(1\text{-}C_8H_{17}NH_3)_2CuCl_4(s)$ as a function of molality m/(mol kg^{-1}) at $T = 298.15$ K

$$V_{\mathrm{m}}(\mathrm{nm}^3) = M_{\mathrm{m}}/\rho N_{\mathrm{A}} = 1.66045 \times 10^{-3} M_{\mathrm{m}}/\rho, \tag{2}$$

where N_{A} is the Avogadro's constant, 6.02245×10^{23} molecule mol^{-1}. Thus, the Eq. 1 is changed to [11]:

$$U_{\mathrm{POT}} = \gamma(\rho/M_{\mathrm{m}})^{1/3} + \delta, \tag{3}$$

where the values of the constants for M_2X (1:2) are: $\gamma = 8375.6$ kJ mol^{-1} cm and $\delta = -178.8$ kJ mol^{-1} [11]; the density ρ (g cm^{-3}) and molar mass M_{m} (g mol^{-1}) are obtained from crystal structure data of the title compound in Table 1, $\rho = 1.253$ g cm^{-3} and $M_{\mathrm{m}} = 465.84$ g mol^{-1},

Table 4 Values of molar dissolution enthalpies of $(1\text{-}C_8H_{17}NH_3)_2CuCl_4(s)$ at various molalities at $T = 298.15$ K

$10^3 m$/mol kg^{-1}	$\Delta_s H_m$/kJ mol^{-1}	$-2m$/mol kg^{-1}	$-4my'$/mol kg^{-1}	Y/K^{-1}
0.864	−4.55236	−0.00173	−0.00317	−0.0035
1.065	−4.22529	−0.00213	−0.00387	−0.00333
1.297	−3.95298	−0.00259	−0.00466	−0.00319
1.510	−3.80559	−0.00302	−0.00538	−0.00313
1.722	−3.6975	−0.00344	−0.00609	−0.00309
1.932	−3.58942	−0.00386	−0.00679	−0.00305
2.157	−3.49818	−0.00431	−0.00752	−0.00302
2.369	−3.40553	−0.00474	−0.00821	−0.00299
2.575	−3.32692	−0.00515	−0.00887	−0.00297
2.783	−3.24832	−0.00557	−0.00953	−0.00294
3.019	−3.16409	−0.00604	−0.01027	−0.00291
3.234	−3.10935	−0.00647	−0.01094	−0.0029
3.446	−3.07426	−0.00689	−0.01159	−0.0029
3.807	−3.05882	−0.00761	−0.0127	−0.00293
4.328	−3.04197	−0.00866	−0.01426	−0.00297

m is the molality of the solute; $\Delta_s H_m$ 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 respectively. V_m is calculated to be 0.6173 nm^3 according to Eq. 2, consequently lattice potential energy of (1-$C_8H_{17}NH_3)_2CuCl_4$ is derived to be $U_{POT} = 986.01$ kJ mol^{-1}.

Molar enthalpy of dissolution at infinite dilution and sum of Pitzer's parameters

(1-$C_8H_{17}NH_3)_2CuCl_4$ can be dissolved in the double-distilled water. The experimental values of enthalpy of dissolution ($\Delta_s H_m$) of (1-$C_8H_{17}NH_3)_2CuCl_4$ in the double-distilled water are given in Table 4, and the curvilinear relationship of $\Delta_s H_m$/(kJ mol^{-1}) with molality *m*/(mol kg^{-1}) is shown in Fig. 3.

The dissolution process of (1-$C_8H_{17}NH_3)_2CuCl_4$(s) may be expressed as:

$$\text{(1-}C_8H_{17}NH_3)_2CuCl_4(s) + WH_2O(l) \longrightarrow$$
$$2(\text{1-}C_8H_{17}NH_3^+)(aq) + Cu^{2+}(aq) + 4Cl^-(aq), \tag{4}$$

where W is the number of kilograms of solvent. Since (1-$C_8H_{17}NH_3)_2CuCl_4$(s) may be dissociated to 2(1-$C_8H_{17}NH_3)^+$(aq), Zn^{2+}(aq), and 4Cl^-(aq) at infinite dilution, G^{ex} can be expressed by Pitzer's unsymmetrical mixing electrolyte solution theory.

The general form of the excess Gibbs energy of electrolytes [12] is given by

$$G^{ex}/(WRT) = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) + \sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk}. \tag{5}$$

The quantities $\lambda_{ij}(I)$ is the second virial coefficients for pairwise interaction between ions i and j, and a function of *I*. The ionic strength dependence may be neglected for the third virial coefficients μ_{ijk} which represent triple ion interactions and are important only at high concentrations. R is the molar gas constant, 8.3145 J mol^{-1} 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 for *f(I)* is given by [12]

$$f(I) = -A_\varphi(4I/b)\ln(1 + bI^{1/2}), \tag{6}$$

where b is a parameter having the value 1.2 kg$^{1/2}$ mol$^{-1/2}$ for all solutions and A_φ is the Debye–Hückel coefficient for the osmotic coefficient given by

$$A_\varphi = (1/3)(2\pi N_0 d_w/1000)^{1/2}(e^2/4\pi\varepsilon_0 DkT)^{3/2}, \tag{7}$$

where D is the dielectric constant or relative permittivity, d_w is the density of the water or other solvent, e is the electronic 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

$$B_{ca} = \lambda_{ca} + |z_X/2z_c|\lambda_{cc} + |z_c/2z_a|\lambda_{aa} \tag{8}$$

$$\theta_{cc'} = \lambda_{cc'} - |z_{c'}/2z_c|\lambda_{cc'} - |z_c/2z_{c'}|\lambda_{cc'} \tag{9}$$

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 [13]. Since the λ depends on the ionic strength, so do B and θ. The following empirical expressions [13] have been found to represent satisfactorily the ionic dependence of B and θ:

$$B_{ca} = \beta_{ca}^{(0)} + (2\beta_{ca}^{(1)}/\alpha^2 I)[1-(1+\alpha I^{1/2})\exp(-\alpha I^{1/2})] \tag{10}$$

$$\theta_{cc'} = \theta_{cc'}^{(0)} + (2\theta_{cc'}^{(1)}/\alpha^2 I)[1-(1+\alpha I^{1/2})\exp(-\alpha I^{1/2})], \tag{11}$$

where the value of α is normally equal to 2.0 kg$^{1/2}$ mol$^{-1/2}$, and $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, $\theta_{ca}^{(0)}$, and $\theta_{ca}^{(1)}$ are characteristic parameters of electrolyte. We substitute Eqs. 8–11 into Eq. 5 and obtain [12]:

$$G^{ex}/(WRT) = f(I) + 2\sum_c \sum_a m_c m_a B_{ca} + 2\sum_c \sum_{c'} m_c m_{c'} \theta_{cc'}. \tag{12}$$

Since the final products of (1-$C_8H_{17}NH_3)_2CuCl_4$(s) dissociation may be [2(1-$C_8H_{17}NH_3)^+$(aq) + Cu^{2+}(aq) + 4Cl^-(aq)] in water and the molality of the sample in dissolution experiment is relatively low, the electrolyte solution may be regarded as an unsymmetrical mixed electrolytes solution: 2(1-$C_8H_{17}NH_3Cl$)-$CuCl_2$ and $m_{[C_8H_{17}NH_3]^+} = 2m$, $m_{Cu^{2+}} = m$, and $m_{Cl^-} = 4m$. Equation 12 can be rewritten as follows:

$$\begin{aligned} G^{ex}/WRT = &-(4A_\varphi I/b)\ln(1 + bI^{1/2}) \\ &+ 4m^2(4\beta^{(0)}_{C_8H_{17}NH_3,Cl} + 2\beta^{(0)}_{Cu,Cl} + \theta_{C_8H_{17}NH_3,Cu}) \\ &+ 8m^2(2\beta^{(1)}_{C_8H_{17}NH_3,Cl} + \beta^{(1)}_{Cu,Cl})y'. \end{aligned} \tag{13}$$

where $y' = [1-(1 + 2I^{1/2})\exp(-2I^{1/2})]/2I$. The equations for the excess enthalpy $L = H^{ex}$ following from temperature differentiation [13] of Eq. 13 can be expressed as

$$\begin{aligned} L = (WRT^2)[&(A_H I/bRT^2)\ln(1 + bI^{1/2}) \\ &- 4m^2(4\beta^{(0)L}_{C_8H_{17}NH_3,Cl} + 2\beta^{(0)L}_{Cu,Cl} + \theta^L_{C_8H_{17}NH_3,Cu}) \\ &- 8m^2(2\beta^{(1)L}_{C_8H_{17}NH_3,Cl} + \beta^{(1)L}_{Cu,Cl})y'] \end{aligned} \tag{14}$$

$$\beta_{ca}^{(0)L} = (\partial\beta_{ca}^{(0)}/\partial T)_P \tag{15}$$

$$\beta_{ca}^{(1)L} = (\partial\beta_{ca}^{(1)}/\partial T)_P \tag{16}$$

$$\theta^L_{cc'} = \left(\partial\theta_{cc'}/\partial T\right)_p \quad (17)$$

$$A_H = 4RT^2(\partial A_\varphi/\partial T)_p \quad (18)$$

where A_H is the Debye–Hückel parameters for enthalpy [14], $A_H = 1986$ J mol^{-1} at $T = 298.15$ K.

From the above equations and the excess enthalpy $L = H^{\mathrm{ex}}$, a working equation [15] to determine the Pitzer's parameter is shown as

$$\begin{aligned} Y = {} & \Delta_s H_m/2RT^2 - (1/2m)\left(A_H I/1.2RT^2\right)\ln(1+1.2I^{1/2}) \\ = {} & \alpha_0 - 2m(4\beta^{(0)L}_{\mathrm{C_8H_{17}NH_3,Cl}} + 2\beta^{(0)L}_{\mathrm{Cu,Cl}} + \theta^L_{\mathrm{C_8H_{17}NH_3,Cu}}) \\ & -4my'(2\beta^{(1)L}_{\mathrm{C_8H_{17}NH_3,Cl}} + \beta^{(1)L}_{\mathrm{Cu,Cl}}) \end{aligned} \quad (19)$$

where Y is the extrapolation function, $\alpha_0 = \Delta_s H^\infty_m/(2RT^2)$. The values of Y, $-2m$, and $-4my'$ are given in Table 4, respectively. The 3D chart of Y against $-2m$ and $-4my'$ is plotted in Fig. 4. Regression of Y against $-2m$ and $-4my'$ is made by least-squares to obtain $\alpha_0 = -4.04 \times 10^{-3}$, $(4\beta^{(0)L}_{\mathrm{C_8H_{17}NH_3,Cl}} + 2\beta^{(0)L}_{\mathrm{Cu,Cl}} + \theta^L_{\mathrm{C_8H_{17}NH_3,Cu}}) = 1.907$ and $(2\beta^{(1)L}_{\mathrm{C_8H_{17}NH_3,Cl}} + \beta^{(1)L}_{\mathrm{Cu,Cl}}) = -1.232$. The standard deviation of fitting is 3.104×10^{-5} and correlation coefficient 0.9727. The molar enthalpy of dissolution for $(1\text{-}C_8H_{17}NH_3)_2CuCl_4(s)$ at infinite dilution is determined to be $\Delta_s H^\infty_m = -5.972\,\mathrm{kJ\,mol^{-1}}$.

The parameters $\beta^{(0)L}_{\mathrm{C_8H_{17}NH_3,Cl}}$, $\beta^{(0)L}_{\mathrm{Cu,Cl}}$, $\beta^{(1)L}_{\mathrm{C_8H_{17}NH_3,Cl}}$, and $\beta^{(1)L}_{\mathrm{Cu,Cl}}$ are attributed to the short-range interaction between the cations and anion. The absolute values of $\beta^{(0)L}_{ca}$ and $\beta^{(1)L}_{ca}$ are very small for the usual electrolyte and have a tendency of increase along with the volume and the quantity of the ion [12]. In this article, the two big values are obtained, $(4\beta^{(0)L}_{\mathrm{C_8H_{17}NH_3,Cl}} + 2\beta^{(0)L}_{\mathrm{Cu,Cl}} + \theta^L_{\mathrm{C_8H_{17}NH_3,Cu}}) = 1.907$ and $(2\beta^{(1)L}_{\mathrm{C_8H_{17}NH_3,Cl}} + \beta^{(1)L}_{\mathrm{Cu,Cl}}) = -1.232$. This shows that various types of strong short-range interactions exist between cations and anions in the solution obtained from dissolution of the complex $(1\text{-}C_8H_{17}NH_3)_2CuCl_4$.

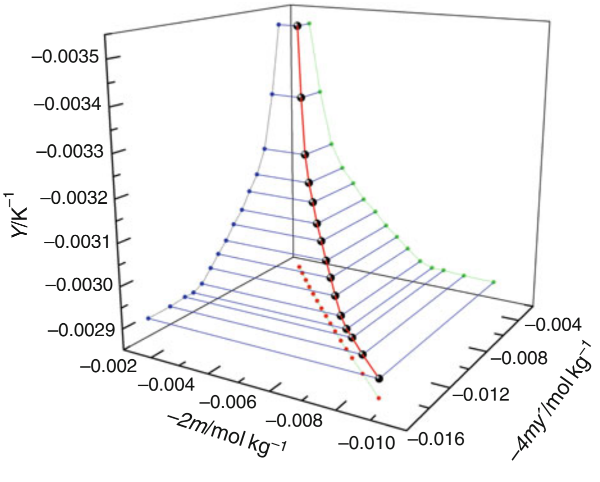

Fig. 4 The 3D chart of Y against $-2m$ and $-4my'$ for $(1\text{-}C_8H_{17}NH_3)_2CuCl_4(s)$

The degree of chaos or disorder of $(1\text{-}C_8H_{17}NH_3)_2CuCl_4$ is increased when $(1\text{-}C_8H_{17}NH_3)_2CuCl_4(s)$ is dissolved in the double-distilled water. It is concluded that the entropy change of dissolution reaction is greater than zero according to the statistical explanation of the entropy in statistical thermodynamics. From the values of enthalpy of dissolution, we deduce that the dissolution of $(1\text{-}C_8H_{17}NH_3)_2CuCl_4(s)$ in the water is a typical exothermic process [16], which indicates that it should be an enthalpy-driven as well as entropy-driven process.

Conclusions

Bis(1-octylammonium) tetrachlorocuprate $(1\text{-}C_8H_{17}NH_3)_2CuCl_4(s)$ is synthesized, and the crystal structure of the compound has been determined by X-ray crystallography. The lattice potential energy is obtained to be $U_{\mathrm{POT}} = 986.01$ kJ mol^{-1} from the crystallographic data. The molar enthalpy of dissolution of $(1\text{-}C_8H_{17}NH_3)_2CuCl_4(s)$ at infinite dilution is determined to be $\Delta_s H^\infty_m = -5.972\,\mathrm{kJ\,mol^{-1}}$ and the sums of Pitzer's parameters are obtained through Pitzer's electrolyte solution theory. The result indicates that it is an exothermic reaction when $(1\text{-}C_8H_{17}NH_3)_2CuCl_4(s)$ is dissolved in the double-distilled water, which indicates that it should be not only an entropy-driven but also an enthalpy-driven process.

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References

1. Jakubas R, Bator G, Gosniowska M, Ciunik Z, Baran J, Lefebvre J. Crystal structure and phase transition of $[(CH_3)_2NH_2]GaCl_4$. J Phys Chem Solids. 1997;58:989–98.
2. Li WP, Zhang DS, Zhang TP, Wang TZ, Ruan DS, Xing DQ, Li HB. Study of solid–solid phase change of $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ for thermal energy storage. Thermochim Acta. 1999;326:183–6.
3. Wu KZ, Zhang JJ, Liu XD. Subsolidus phase diagram of binary system of thermotropic phase transitions compounds $(n\text{-}C_nH_{2n+1}NH_3)_2MnCl_4$ (n = 12, 14, 16). Thermochim Acta. 2009;483:55–7.
4. Kang JK, Choy JH, Madeleine RL. Phase transition behavior in the perovskite-type layer compound $(n\text{-}C_{12}H_{25}NH_3)_2CuCl_4$. J Phys Chem Solids. 1993;54:1567–77.
5. Yang WW, Di YY, Li J, Kong YX. Thermochemistry on ephedrine hydrochloride and *N*-methylephedrine hydrochloride. J Chem Thermodyn. 2009;41:945–50.
6. Dan WY, Di YY, Kong YX, Wang Q, Yang WW, Wang DQ. Crystal structure and solid–solid phase transition of the complex $(C_{11}H_{18}NO)_2CuCl_4(s)$. J Therm Anal Calorim. 2010;102:291–6.

7. Xue BD, Yang Q, Chen SP, Gao SL. Synthesis, crystal structure, and thermodynamics of a high-nitrogen copper complex with *N*,*N*-bis-(1(2)H-tetrazol-5-yl) amine. J Therm Anal Calorim. 2010;101:997–1002.
8. Di YY, Tan ZC, Li LW, Gao SL. Thermochemistry on the coordination compounds of zinc sulphate with several L-a-amino acids. J Chem Thermodyn. 2006;38:884–8.
9. Liu YP, Di YY, Dan WY, He DH, Kong YX, Yang WW. Thermochemistry on dodecylamine hydrochloride and bis-dodecylammonium tetrachlorozincate. J Therm Anal Calorim. 2011;103:987–93.
10. Jenkins HDB, Glasser L. Ionic Hydrates, $M_pX_q{\cdot}nH_2O$: lattice energy and standard enthalpy of formation estimation. Inorg Chem. 2002;41:378–88.
11. Kong YX, Di YY, Yang WW, Lü YF, Tan ZC. Crystal structure, phase transition, and thermodynamic properties of bis-dodecylammonium tetrachlorozincate $(C_{12}H_{25}NH_3)_2ZnCl_4(s)$. Chin J Chem. 2010;28:521–30.
12. Yang JZ, Pitzer KS. Thermodynamics of electrolyte mixtures. Activity and osmotic coefficients consistent with the higher-order limiting law for symmetrical mixing. J Solut Chem. 1988;17:909–24.
13. Phutela RC, Pitzer KS. Thermodynamics of electrolyte mixtures. Enthalpy and the effect of temperature on the activity coefficient. J Solut Chem. 1986;15:649–62.
14. Pitzer KS. Activity coefficients in electrolyte solutions. 2nd ed. Boca Raton: CRC Press; 1991. p. 75–153.
15. Pitzer KS. Thermodynamics of unsymmetrical electrolyte mixtures. Enthalpy and heat capacity. J Phys Chem. 1983;87:2360–4.
16. Yang WW, Di YY, Kong YX, Tan ZC. Low-temperature heat capacities and standard molar enthalpy of formation of pyridine-2,6-dicarboxylic acid. Chin Phys B. 2010;19:060517-1–7.