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Crystal structures and solid–solid phase transitions on phase change materials $(1-C_nH_{2n+1}NH_3)_2CuCl_4(s)$ ($n=10$ and 11)

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ABSTRACT

Two novel crystalline complexes $(C_{10}H_{21}NH_3)_2CuCl_4(s)$ and $(C_{11}H_{23}NH_3)_2CuCl_4(s)$ (abbreviated as $C_{10}Cu(s)$ and $C_{11}Cu(s)$), which may be used as the phase change materials, were synthesized by liquid phase reaction. Crystal structures and chemical compositions of the two complexes were determined by X-ray single crystal diffraction technique, chemical analysis and elemental analysis. Low-temperature heat capacities of the two new phase change materials were measured by a precise automatic adiabatic calorimeter in the temperature range from 78 to 395 K. The temperatures, molar enthalpies and entropies of the phase transitions for each of the two complexes were determined to be: for $(C_{10}Cu(s))$, 310.64 ± 0.05 K, 81.12 ± 0.11 kJ/mol, and (261.24 ± 0.06) J/K mol for the first peak, 315.17 ± 0.04 K, 10.17 ± 0.52 kJ/mol, and 32.28 ± 1.66 J/K mol for the second peak; for $(C_{11}Cu(s))$, they were 311.39 ± 0.69 K, 70.17 ± 0.25 kJ/mol, and 225.36 ± 0.66 J/K mol for the first peak, 321.85 ± 0.46 K, 10.58 ± 0.26 kJ/mol, and $32.86\pm$ 0.07 J/K mol for the second peak, respectively. Two polynomial equations of the heat capacities as a function of temperature were fitted by the least-square method. Smoothed heat capacities and thermodynamic functions of the two phase change materials were calculated based on the fitted polynomial equations. In addition, the solid–solid phase transitions and melting processes of the two complexes were verified by DSC and TG techniques, and the reversibility and repeatability of the two phase transitions for each of the two complexes were discussed.

1. Introduction

Protecting the environment is an important task throughout the world. A major requirement of green economy is to produce and utilize the eco-friendly energy. Nowadays, energy crisis is threatening the whole world. Contribution of energy to societal development is obvious, but much trouble has been and is being brought to mankind by the unreasonable use of energy resulting in the increasingly serious environmental pollution. Therefore, green energy as an environment-friendly energy is urgently demanded by human and society. In order to develop a new green energy and reduce the environmental pollution and waste of energy, the improvement of utilization rate of energy source in the modern world has attracted much attention. For the purpose, the use of phase change materials (PCMs) [1–3] has gained the considerable importance in optimal utilization of energy.

The PCMs are also known as latent thermal energy storage materials, which is friendly to the environment. They can be used as low carbon building materials in the new city construction because of no discharge and pollution, which not only matches with low carbon life, but also is good for the global climate. A variety of PCMs available in practice are well known for their thermodynamic properties. These materials can be encapsulated by a polymer cover and exist in the market [4–5].

In principle, PCMs can be used as a solar energy material if the temperature range of the phase transition is suitable and the enthalpy of the phase transition is enough large. In recent decades, the solid–solid phase change materials (SSPCMs) [6–8] have become one of the most promising functional materials because of its excellent performance of energy storage and release, such as small change in volume, no volatilization, shape plasticity and so on.

As a kind of solid–solid phase change materials, plenty of studies [9–10] about the complexes $(1-C_nH_{2n+1}NH_3)_2MX_4$ are reported, in which M is a divalent transition metal ion ($M=Zn^{2+}$, Cu^{2+}, Mn^{2+}, Cd^{2+}, Co^{2+}, etc.), X is a halogen, and n varies between 8 and 18. $(1-C_nH_{2n+1}NH_3)_2MX_4$ have a lot of advantages. They can be conveniently applied in many fields such as solar energy utilization, temperature controlling greenhouses, technology of peak load shifting, waste heat recovery, energy efficient air conditioning and so on [11–15].

The adiabatic calorimetry can be applied to study the solid–solid phase transitions by measuring low temperature heat capacities and calculating relevant thermodynamic data. In this

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article, we synthesize two new crystalline complexes $C_{10}Cu(s)$ and $C_{11}Cu(s)$ via the liquid phase reaction. With X-ray single crystal diffraction technique, chemical analysis and element analysis, crystal structures and compositions of the two complexes are determined. Low-temperature heat capacities of $C_{10}Cu(s)$ and $C_{11}Cu(s)$ are measured by a precise automatic adiabatic calorimeter in the temperature range from 78 to 395 K and their thermodynamic properties are derived. The solid to solid phase transitions are investigated by the analysis of heat capacity curves of the two complexes. Further, the solid–solid phase transitions and the melting processes of the two complexes are verified by DSC and TG techniques.

2. Experimental

2.1. Synthesis and characterization of $(1-C_nH_{2n+1}NH_3)_2CuCl_4(n=10$ and 11)

1-Decylamine, 1-undecylamine, hydrochloric acid (37% in mass percent) and copper chloride dihydrate as the reactant, and anhydrous methyl alcohol as the solvent are all of analytical grade, and all of them are purchased from J&K Scientific Ltd., China. The reactants are accurately weighed at the molar ratio of $n(C_nH_{2n+1}NH_2)$: n(hydrochloric acid): $n(CuCl_2\cdot 2H_2O)=2:2:1$, where hydrochloric acid is slightly excessive and slowly dissolved in anhydrous methyl alcohol. The mixture is heated by an electric jacket, stirred under boiling, and refluxing for 4 h. The final solution is laid aside, and several days later, the golden-yellow transparent crystals are obtained. The crystals are washed three times by ether and recrystallized three times by anhydrous methyl alcohol. Finally, the sample is placed in a vacuum desiccator at $T=300$ K to dry in vacuum for 6 h. The final product is put in a weighing bottle and preserved in a desiccator. Theoretical contents of C, H, N, Cu, and Cl in the complex $C_{10}Cu_4(s)$ are calculated to be 47.29%, 9.52%, 2.76%, 12.51% and 27.92%, and for $C_{11}Cu(s)$, they are 49.30%, 9.78%, 2.61%, 11.85% and 26.46%, respectively. Chemical and elemental analysis (model: PE-2400, Perkin Elmer, USA) show that the practical contents of C, H, N, Cu, and Cl in the complex $C_{10}Cu(s)$ are measured to be 47.26%, 9.54%, 2.75%, 12.52% and 27.93%, and for $C_{11}Cu(s)$, they are 49.32%, 9.76%, 2.60%, 11.84% and 26.48%, respectively. These results show that the purities of the two samples prepared are >0.995 in mass fraction.

X-ray crystallography is applied to characterize crystal structures of the two complexes. A crystal is glued to a fine glass fiber and then mounted on the Bruker Smart-1000 CCD diffractometer with Mo-Kα radiation, $\lambda=0.71073$ Å. The intensity data are collected in the φ–ω scan mode at $T=298(2)$ K. The empirical absorption corrections are based on multi-scan. The structures are solved by direct method and different Fourier syntheses, and all non-hydrogen atoms are refined anisotropically on F^2 by the full-matrix least-square method. All calculations are performed with the program package SHELXTL [16].

The crystal data and details of data collection and refinements for the two complexes are summarized in Table 1. The selected bond lengths and angles for them are listed in Table 2. The hydrogen bond lengths and angles are presented in Table 3. We have applied for two CCDC numbers 833345 for $C_{10}Cu(s)$ and 833346 for $C_{11}Cu(s)$.

2.2. Adiabatic calorimetry

A precise automatic adiabatic calorimeter is used to measure heat capacities of the two compounds in the temperature range from 78 to 395 K. The calorimeter is established in Thermochemistry Laboratory, Liaocheng University, China. The principle and performance of the adiabatic calorimeter and the procedures of heat capacity measurements have been described in detail elsewhere [17]. Heat-capacity measurements are continuously and

Table 1
Crystallographic data and structure refinements for $(1-C_nH_{2n+1}NH_3)_2CuCl_4(s)(n=10$ and 11).

Properties	Crystallographic data and structure refinements	
Empirical formula	$(C_{10}H_{21}NH_3)_2CuCl_4$	$(C_{11}H_{23}NH_3)_2CuCl_4$
Formula weight	521.94	550.00
Temperature	298(2) K	298(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	P–1	P–1
Unit cell dimensions	$a=7.2394(9)$ Å;	$a=7.2470(7)$ Å
	$b=7.5675(11)$ Å;	$b=7.5570(8)$ Å
	$c=25.631(2)$ Å;	$c=27.421(3)$ Å
	$\alpha=83.7520(10)^\circ$;	$\alpha=96.038(2)^\circ$
	$\beta=87.9180(10)^\circ$	$\beta=91.0100(10)^\circ$
	$\gamma=89.988(2)^\circ$	$\gamma=90.3230(10)^\circ$
Volume	1394.9(3) Å^3	1493.1(3) Å^3
Z	2	2
Calculated density	1.243 g/cm^3	1.223 g/cm^3
Absorption coefficient	1.174 mm^{-1}	1.101 mm^{-1}
$F(000)$	558	590
Crystal size	$0.50\times0.48\times0.43$ mm^3	$0.48\times0.47\times0.06$ mm^3
θ range for data collection	1.60–25.02°	2.71–25.02°
Limiting indices	$-8\le h\le 5$, $-8\le k\le 9$, $-30\le l\le 29$	$-8\le h\le 8$, $-7\le k\le 8$, $-32\le l\le 32$
Reflections collected/unique	7237/4836 [R(int)=0.0493]	7814/5197 [R(int)=0.0576]
Completeness to $\theta=25.02$	98.2%	98.6%
Max. and min. transmission	0.6321 and 0.5913	0.9369 and 0.6201
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4836/0/268	5197/19/269
Goodness-of-fit on F^2	1.042	1.032
Final R indices [$I>2$sigma(I)]	$R_1=0.0628$, $wR_2=0.1558$	$R_1=0.0613$, $wR_2=0.1244$
R indices (all data)	$R_1=0.0978$, $wR_2=0.1848$	$R_1=0.1084$, $wR_2=0.1365$
Largest diff. peak and hole	0.951 and -0.919 e/Å^3	1.150 and -0.474 e/Å^3