Metal Complexes of π-Expanded Ligands (8): Cold Crystallization of bis[2-[(octylimino)methyl]-1-pyrenolato-N,O] copper(II) by Thermal Analyses, Magnetic Studies, and FT-IR

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ARTICLE INFO
Received: 14/2/2021
Accepted: 15/3/2021
Keywords:
Polymorphism, Copper, Pyrene, π-Expanded ligand, Salicylaldimine

ABSTRACT
Molecules exhibiting cold crystallization, an exothermic phenomenon in heating following supercooling, can be used as a heat-storing material. On the other hand, examples in non-polymers are still few. To test metal complexes as potential compounds for heat-storage materials, a salicylaldiminate-typed copper(II) complex, bis[2-[(octylimino)methyl]-1-pyrenolato-N,O] copper(II) 1(Cu), which had two different coloured forms and a characteristic long alkyl chain, exhibited complicated thermal behaviour including cold crystallization. The long alkyl chain was a steric barrier to molecular stacking, leading to the supercooled state. Besides, the two polymorphs were characterized by IR spectra studies and magnetic susceptibility.

Introduction

Nowadays, the use of thermal energy is essential for the improvement in energy efficiency.1 To achieve this, emerging technologies for storage,2 exchange,3 extraction,4 and others are necessary.5 The advantage of thermal storage is to eliminate the time lag between the supply and demand of heat. Recently, Saito et al. proposed the combination of glass transition and cold crystallization as a protocol to improve the controllability of heat-storage/release.5,6 The assumed scenario is as follows. The heat-storage material melts during the first heating process. On cooling the liquid, it shows supercooling, followed by a glass transition at the glass transition temperature (Tg), below which the glass is kinetically “stable.” On reheating, this glass exhibits softening around Tg. Above Tg, the material is transformed from a supercooled liquid to a crystal.

Therefore, the heat release on cold crystallization is the key to using supercooled liquids for thermal storage with desired controllability.5,6

The use of the change in coordination bonds, the energy of which lies in between van der Waals interaction used in thermophysical heat-storage7-10 and covalent bonds in thermochemical storage,11-15 would lower the working temperature while maintaining relatively high energy density. In this context, it is worthwhile to develop compounds exhibiting the cold crystallization accompanied by a change in the coordination mode. Within the various materials exhibiting a cold crystallization (polymer,16-18 ionic liquid,19 organic material,20 and metal complexes5,6,21), a Schiff-base metal complex, bis[N-(2-propyl)-5,6-benzosalicylideneaminato]nickel(II) reported by Wang et al.21 They reported i) a colour change, probably caused by a change in the coordination structure from
square planar (green) to tetrahedral (brown), and ii) a cold-crystallization phenomenon.

Inspired by this, the author began the study on similar compounds and reported the cold crystallization in bis[2-[(octylimino)methyl]-1-pyrenolato-N,O] copper(II) 1(Cu) with the possible molecular origin of its cold crystallization.5,6,21 In this report, the cold crystallization of bis[2-[(octylimino)methyl]-1-pyrenolato-N,O] copper(II) is studied and discussed using the magnetic properties, the FT-IR spectra, and thermal analyses.

**Experimental**

Synthesis of bis[2-[(octylimino)methyl]-1-pyrenolato-N,O] copper(II) 1(Cu), C₅₀H₃₂CuN₅O₂.2₂°2₉

A mixture of 1-hydroxy-2-[(octylimino)methyl]-pyrene 1 (30.05 mg, 0.084mmol), anhydrous CH₃COONa (26.28 mg, 0.32mmol) in 6 mL of mixture of toluene and ethanol (PhMe/EtOH = 5:1) was added Cu(CH₃COO)₂·H₂O (8.35 mg, 0.042 mmol) at 60 °C. The mixture was stirred for 3 h. After a fast cool-down with an ice bowl, the reaction mixture was filtered and the residue was washed with methanol to obtain 1(Cu) as a yellow solid (26.64 mg, 82%). Mp: 192 °C; IR(KBr) (cm⁻¹) 1616 (C=N). UV/vis (PhCH₃) λ_max/μm (ε/M⁻¹ cm⁻¹) 483 (15,793), 460 (15,599), 385 (78,576), 366 (shoulder, 43,689), 302(81,553). HR-MS (m/z): [M⁺] Calcd for C₅₀H₃₂CuN₅O₂: 776.34; Found: 776.34. Anal. Calcd for C₅₀H₃₂CuN₅O₂: C, 77.34; H, 6.75; N, 3.61. Found: C, 77.17; H, 6.95; N, 3.45.

Zero-field cooled magnetic susceptibility was measured in the temperature range of 2-300 K for the complex. Measurements were performed at 5000 Oe, using a Quantum Design Squid susceptormeter-magnetometer She 906. The susceptibility data were corrected by the diamagnetic contributions using the Pascal constants.26 The phase transition behaviour of the complexes was investigated using a commercial differential scanning calorimeter (DSC) (Mettler Toledo, DSC-1). Open pans of aluminium were used under a nitrogen gas (100 mL min⁻¹). The scanning rates were 5.0 °C min⁻¹. Onset temperatures of anomalies in DSC traces were adopted as transition temperatures. Infrared spectra were recorded on a Shimadzu FTIR-8400 instrument using the KBr pellet and/or liquid-film techniques in the range of 500 to 4000 cm⁻¹.

**Results and discussion**

*Preparation of two polymorphs*

Scheme 1 exhibits two different thermal processes to obtain two polymorphs of the Cu(II) complex 1(Cu). The preparation of these polymorphs includes two steps, (1) remove any remaining copper acetate and sodium acetate (by column chromatography) to give crude 2; (2) thermal treatment with the different solvent. After preparing two polymorphs of the copper complex 1(Cu), elemental analyses and mass spectra studies supported the formation of two polymorphs of 1(Cu) in different colours.

**Thermal studies on the two polymorphs**

The complex 1(Cu) phase-transition behaviour was investigated utilizing a commercial differential scanning calorimeter (DSC). Open pans of aluminium were used under a nitrogen gas (100 mL min⁻¹). Transition temperatures were determined as onset temperatures. Figure 1 and Figure 2 show DSC curves of black form and yellow form, respectively. Herein, Run 1 and Run 3 are the first heating process and the second heating process of each form of 1(Cu) that have the melting point, and Run 2 and Run 4 are the first cooling process and the second cooling process of each form of 1(Cu) that have the crystallization point. As shown in https://doi.org/10.51316/jca.2021.022
these figures, the melting points were observed at 192.3°C and 188.8 °C for black form and yellow form, respectively. After the second cooling (Run-4), essentially the same behaviour as Run-1 and Run-2 was observed. The cold crystallization point (C) was only exhibited at Run-3 of yellow form of 1(Cu).

Through these data, the author believes that the yellow polymorph is kinetically favored and the black polymorph is thermodynamically favored.

Figure 1: DSC traces of black form of the copper complex 1(Cu) measured under nitrogen with a scanning rate of 5.0 °C

Figure 2: DSC traces of yellow form of the copper complex 1(Cu) measured under nitrogen with a scanning rate of 5.0 °C
Magnetic studies on the two polymorphs

Figure 3 shows the temperature dependence of magnetic susceptibility $\chi_A$ and effective magnetic moment $\mu_{\text{eff}}$ measured in the magnetic field of 5000 Oe as a function of temperature in the range of 2-300 K for two polymorphs of the complex $1(Cu)$ in the solid-state. The plot of $1/\chi_A$ versus $T$ for $T > 50$ K obeys the Curie-Weiss law, where the Weiss constant is the negative value of $\theta = -0.2$ K. In the range of the temperature mentioned above, the effective magnetic moment $\mu_{\text{eff}}$ is in the range of 1.73-2.13 $\mu_B$ showing one unpaired electron, a d$^9$ configuration, on the copper center in the monomer complex $1(Cu)$. The slight decrease of $\mu_{\text{eff}}$ below 20 K, the small value of the Weiss constant, and the obtained coupling constant $J = 0.0$ cm$^{-1}$ show no interaction between the copper monomers that is expected for the copper center separated by the large distance (> 8 Å).$^{26}$

As shown in Figure 3, the effective magnetic susceptibilities $\mu_{\text{eff}}$ of both polymorphs are slightly different.

IR spectra studies on the two polymorphs

Figure 4. IR spectra for KBr tablets of two polymorphs of copper complex $1(Cu)$ in various regions, black form (red line) and yellow form (blue line)

As suggested by Ebert and Gottlieb, yellow form and black form could be easily distinguished using IR.$^{5,6,21}$ Expanded solid IR spectra (KBr method) are shown in Figure 4. The significant differences were found in the area of 1200-1600 cm$^{-1}$ in which vibration of the aromatic C=C bond occurs. The peaks that
characterized the two polymorphic forms, black and yellow, are summarized in Table 1.

Table 1: Solid IR assignments and comparison of wavenumber peaks (cm⁻¹) of two polymer-phisms, black form and yellow form, of the copper(II) complex 1(Cu)

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Black form</th>
<th>Yellow form</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H stretching vibrations</td>
<td>2957, 2924, 2855</td>
<td>2954, 2926, 2855</td>
</tr>
<tr>
<td>C=N stretching vibrations</td>
<td>1614</td>
<td>1616</td>
</tr>
<tr>
<td>Aromatic C=C stretching vibrations</td>
<td>1540, 1473</td>
<td>1540, 1473</td>
</tr>
<tr>
<td>C-H in-plane bending vibrations</td>
<td>1224, 1184</td>
<td>1223, 1190</td>
</tr>
<tr>
<td>C-H out-of-plane bending vibrations</td>
<td>842, 758, 684</td>
<td>841, 758, 686</td>
</tr>
</tbody>
</table>

Conclusion

We considered the possibility of utilizing metal complexes as heat-storage materials, and we prepared the two isomers of salicylaldiminato-typed copper(II) complexes derived from pyrene. The cold crystallization behaviour of the isomers was studied using magnetic properties, thermal and spectroscopic analyses. The long alkyl chain was a steric barrier to molecular stacking, leading to the supercooled state. Although it is difficult to do so for the present compound, such compounds could be used to develop heat-storage materials with large "heat" capacities.

Acknowledgments

This work was supported in part by the Priority Research Program sponsored by the Asian Human Resources Fund from Tokyo Metropolitan Government (TMG), a research grant funded by Vietnam Ministry of Education and Training (Grant No. B2021-BKA-19), and a research grant funded by Vietnam Electricity Power Generation Corporation 1 (Grant No. 84/HK-CN-EVNGENC01-BKHN). L.X.D. appreciates Tokyo Metropolitan University (TMU) for a pre-doctoral fellowship. The author appreciates the scientific and supervision support of Ken-ichi Sugiuira and Ken-ichi Yamashita (TMU), the magnetic measurement of Masaaki Ohba (Kyushu University), and the elemental analyses of Mr. Toshihiko Sakurai (TMU).

References


