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Crystal structure and solid–solid phase transition of the complex $(C_{11}H_{18}NO)_2CuCl_4(s)$

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Abstract The complex $(C_{11}H_{18}NO)_2CuCl_4(s)$ was synthesized. Chemical analysis, elemental analysis, and X-ray crystallography were used to characterize the structure and composition of the complex. Low-temperature heat-capacities of the compound were measured by an adiabatic calorimeter in the temperature range from 77 to 400 K. A phase transition of the compound took place in the region of 297–368 K. Experimental molar heat-capacities were fitted to two polynomial equations of heat-capacities as a function of the reduced temperature by least square method. The peak temperature, molar enthalpy, and entropy of phase transition of the compound were calculated to be $T_{trs} = 354.214 \pm 0.298$ K, $\Delta_{trs}H_m = 76.327 \pm 0.328$ kJ mol^{-1}, and $\Delta_{trs}S_m = 51.340 \pm 0.164$ J K^{-1} mol^{-1}.

Keywords $(C_{11}H_{18}NO)_2CuCl_4(s)$ · X-ray crystallography · Crystal structure · Adiabatic calorimetry · Low-temperature heat-capacity · Solid–solid phase transition

Introduction

N-methylephedrine ($C_{11}H_{17}NO$) (CAS registry number is 552-79-4) can relax bronchial smooth muscle and is a crude material in the production of the drug curing the tracheitis and rheum [1]. Chemical name of the compound is (1R, 2S)-2-dimethylamino-1-phenylpropanol. Recently, it is found that the coordination compounds of *N*-methylephedrine with some transition or biologically active metals can greatly enhance the curing effect of the drug. These medicines synthesized as complexes have a wide perspective since they have no toxicity, high efficiency, and no side effect in the human body. It is well-known that copper is one of trace elements necessary for human, animals, and plants. It has important physiological functions and nutritional values, and participates in many metabolic processes of cells in the biological body. It is intimately related to more than 30 kinds of enzymes in human body and promotes growth and development of tissues. The shortage of the copper in human body may result in many kinds of diseases including sugar diabetes and cardiovascular diseases. The complex of *N*-methylephedrine with cupric chloride may be used as a compound medicine. Crystal structure and thermodynamic properties of a substance are closely concerned with other physical, biological, physiological, and chemical properties [2, 3]. However, crystal structure and thermodynamic properties of the title compound have not been reported in the literature. These results are necessary to develop new application fields of the compound, to improve the techniques of chemical synthesis in which it participates, and to carry out relevant theoretical research. A precise automated adiabatic calorimeter is one of the basic devices necessary for some thermochemical research of matter, especially for phase transition process of material [4]. For these purposes, in the present work, crystal structure of the substance has been determined by X-ray crystallography, low-temperature heat-capacities were measured by the precise automated adiabatic calorimeter. Eventually, some thermodynamic parameters of the solid–solid phase transition of the complex were calculated using the experimental results.

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Experimental

Synthesis and characterization of the complex $(C_{11}H_{18}NO)_2CuCl_4(s)$

N-methylephedrine hydrochloride ($C_{11}H_{18}NOCl$) and cupric chloride used as the reactants were of analytical grade with a labeled purity of more than 99.5% and accurately weighed at the molar ratio of $n(C_{11}H_{18}NOCl):n(CuCl_2) = 2:1$. Certain amount of *N*-methylephedrine hydrochloride (about 20 mmol) was first dissolved in 80 cm^3 of anhydrous ethanol in a 250 cm^3 flask. A solution of anhydrous cupric chloride (about 10 mmol) in anhydrous ethanol (40 cm^3) was added slowly. The mixture was heated and stirred under reflux for 6 h. Then, the above solution was heated and condensed on the electric furnace till crystal membrane appeared. The final solution was naturally cooled to room temperature, filtered, and the crude product was washed by anhydrous ethanol for three times. The blue solid product was recrystallized using anhydrous ethanol, and bright blue crystals were obtained. Finally, the sample was placed in a vacuum desiccator to vacuum dry for 6 h. Theoretical contents of Cu, C, Cl, O, H, and N in the compound have been calculated to be 11.23, 46.70, 25.06, 5.65, 6.41, and 4.95%, respectively. Chemical and element analysis (model: PE-2400, Perkin Elmer, USA) have shown that practical contents of Cu, C, H, and N in the compound have been measured to be 11.20, 46.68, 6.42, and 4.93%, respectively. The above result showed that the purity of the sample prepared was higher than 99.50 mol%. The content of copper in the sample was measured by EDTA complex titration. It was demonstrated from results of chemical analysis that no crystal H_2O exists in the coordination compound.

X-ray crystallography

A crystal with dimensions of 0.24 mm × 0.17 mm × 0.07 mm was glued to a fine glass fiber and was then mounted on the Bruker Smart-1000 CCD diffractometer with Mo–K_α 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 SHELXL-97 program [5]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. The hydrogen atoms were added theoretically, which rided on the concerned atoms, and were not refined.

Adiabatic calorimetry

A precise automatic adiabatic calorimeter was used to measure heat-capacities of the compound over the temperature range from 77 to 400 K. 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 [3, 6]. 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 middle shields, and between the middle and 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 on line 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 from 77 to 400 K. 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 mol^{-1}. Relative deviations of the experimental results from those of the smoothed curve lie within ±0.29%, while the uncertainty is ±0.3%, as compared with the values given by the former National Bureau of Standards [7] 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 0.1–0.4 K min^{-1} and 1–3 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}–10^{-4} K 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 [6]. The sample mass used for calorimetric measurements was 2.1386 g, which was equivalent to 0.0038 mol in terms of its molar mass, $M = 565.87$ g mol^{-1}.

Results and discussion

Crystal structure

The molecular structure of $(C_{11}H_{18}NO)_2CuCl_4(s)$ is shown in Fig. 1. Crystal data and refinement details are

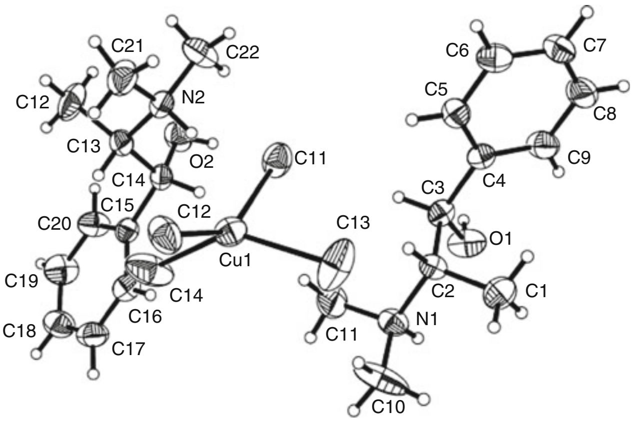

Fig. 1 Structure of the title compound $(C_{11}H_{18}NO)_2CuCl_4(s)$

Table 1 Crystal data and structure refinement for the complex $(C_{11}H_{18}NO)_2CuCl_4(s)$

Crystallographic data	Structure refinement
Empirical formula	$C_{22}H_{36}Cl_4CuN_2O_2$
Formula weight	565.87
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	$a = 12.750(2)$ Å, $b = 8.648(2)$ Å, $c = 13.338(3)$ Å; $\alpha = 90°$, $\beta = 107.987(2)°$, $\gamma = 90°$
Volume	1398.9(5) $Å^3$
Z	2
Calculated density	1.343 g/cm^3
Absorption coefficient	1.183 mm^{-1}
$F(000)$	590
Crystal size	0.24 mm × 0.17 mm × 0.07 mm
θ range for data collection	1.61°–25.01°
Limiting indices	$-15 \leq h \leq 11$, $-10 \leq k \leq 8$, $-15 \leq l \leq 15$
Reflections collected/unique	7038/4471 [R(int) = 0.0291]
Completeness to theta = 25.01	99.7%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4471/61/282
Goodness-of-fit on F^2	0.996
Final R indices [$I > 2$ sigma (I)]	$R_1 = 0.0393$, $wR_2 = 0.0766$
R indices (all data)	$R_1 = 0.0643$, $wR_2 = 0.0836$
Absolute structure parameter	−0.002(15)
Largest diff. peak and hole	0. 312 and −0.286 e $Å^{-3}$

Table 2 Selected bond lengths/Å and angles/° for the complex $(C_{11}H_{18}NO)_2CuCl_4(s)$

Cu(1)–Cl(1)	2.2389(15)	Cl(2)–Cu(1)–Cl(4)	99.13(6)
Cu(1)–Cl(2)	2.2381(15)	Cl(3)–Cu(1)–Cl(4)	141.26(7)
Cu(1)–Cl(3)	2.2407(14)	Cl(2)–Cu(1)–Cl(1)	142.66(6)
Cu(1)–Cl(4)	2.2532(15)	Cl(3)–Cu(1)–Cl(1)	95.23(5)
N(1)–C(2)	1.523(5)	Cl(4)–Cu(1)–Cl(1)	94.80(5)
N(1)–C(10)	1.484(6)	Cl(2)–Cu(1)–Cl(3)	95.16(5)
N(1)–C(11)	1.487(6)	C(3)–O(1)–H(1)	109.5
N(2)–C(13)	1.510(5)	C(14)–O(2)–H(2)	109.5
N(2)–C(21)	1.483(6)	C(21)–N(2)–H(2A)	105.7
N(2)–C(22)	1.492(6)	N(2)–C(21)–H(21A)	109.5
N(1)–H(1A)	0.9100	N(2)–C(21)–H(21B)	109.5
N(2)–H(2A)	0.9100	H(21A)–C(21)–H(21B)	109.5
O(1)–C(3)	1.407(5)	N(2)–C(21)–H(21C)	109.5
O(1)–H(1)	0.8200	O(1)–C(3)–C(4)	115.4(4)
O(2)–H(2)	0.8200	O(1)–C(3)–C(2)	105.7(3)
O(2)–C(14)	1.422(6)	C(4)–C(3)–C(2)	110.5(4)

summarized in Table 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 $a = 12.750(2)$ Å, $b = 8.648(2)$ Å, $c = 13.338(3)$ Å; $\alpha = 90°$, $\beta = 107.987(2)°$, $\gamma = 90°$, respectively. The crystal structure of the coordination compound is monoclinic and the space group is $P2_1$, as shown in Table 1. The copper atom is four-coordinate in a distorted tetrahedron geometry. The four chlorine atoms coordinate with a center copper atom. The coordination ion $(CuCl_4)^{2-}$ and two outer ions $(C_{11}H_{18}NO)^+$ hold together by electrovalent bond. The packing of structure of the title compound is "sandwich" system, which is formed by hydrogen bonds (N–H···Cl, O–H···Cl), i.e., each inorganic layer is sandwiched between two organic layers, as seen in Fig. 2. In addition, π–π interactions exist in neighboring phenyl groups. The combination of these hydrogen bonds with π–π stacking interactions leads to the formation of a two-dimensional network of the title complex.

Low-temperature heat-capacities

The experimental molar heat-capacities of the coordination compound are listed in Table 4 and plotted in Fig. 3. An obvious endothermic peak appears in the temperature region from 297 to 368 K. The melting point is measured to be 182.5–184.5 °C by a melting point apparatus. TG/DTG shows that no mass loss took place in the temperature region of the phase transition. The endothermic peak is attributed to a solid–solid phase transition of the sample from one crystalline state to another noncrystalline state, which has been verified by the data of infrared spectrum. The break of hydrogen bonds (N–H···Cl, O–H···Cl) and the order–disorder transition of the rigid group in the crystal complex may result in the phenomenon of the solid–solid phase transition. Similar explanations have been reported in previous paper [8].

Table 3 Hydrogen bonds for the complex $(C_{11}H_{18}NO)_2CuCl_4(s)$

D–H···A	d(D–H)/Å	d(H···A)/Å	<DHA/°	d(D···A)/Å	Symmetry code of acceptor atom
N(1)–H(1A)···Cl(4)	0.910	2.487	141.73	3.252	$[-x + 2, y - 1/2, -z + 1]$
N(2)–H2(A)···Cl(1)	0.910	2.277	151.74	3.108	–
O(1)–H(1)···Cl(3)	0.820	2.309	167.50	3.115	$[x, y - 1, z]$
O(2)–H(2)···Cl(2)	0.820	2.490	148.45	3.218	$[x, y - 1, z]$

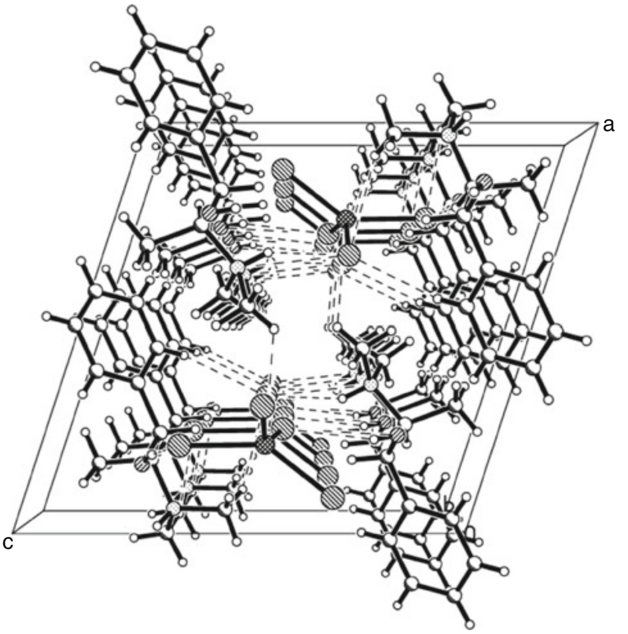

Fig. 2 Packing of structure of the title compound $(C_{11}H_{18}NO)_2CuCl_4(s)$

The experimental points in the temperature regions between $T = 77$ and 297 K and between $T = 368$ and 400 K are, respectively, fitted by the least square method, and two polynomial equations of the experimental molar heat-capacities ($C_{p,\mathrm{m}}$) versus reduced temperature (X), $X = f(T)$, have been obtained.

Before the solid–solid phase transition in the temperature range from $T = 77$ to 297 K,

$$C_{p,\mathrm{m}}/\mathrm{J\,K^{-1}\,mol^{-1}} = 433.127 + 209.818X + 25.010X^2 + 29.621X^3 - 28.684X^4 \tag{4}$$

in which $X = (T/\mathrm{K}—187)/110$. The correlation coefficient for the fitting R^2 equals 0.99994. The value, 187, is half of the upper limit 297 K plus the lower limit 77 K in the temperature range of 77–297 K, while 110 is half of the upper limit 297 K minus the lower limit 77 K in the same range. The reduced temperature (X) obtained using the method are between +1 and −1, and 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.

The above Eq. 4 is valid in a temperature range of 77–297 K. The relative deviations of the smoothed heat-capacities obtained by the above equation from experimental heat-capacities were within ±0.5% except for one point around lower temperature limit, as shown in Fig. 4.

After the solid–solid phase transition in the temperature range from $T = 368$ to 400 K,

$$C_{p,\mathrm{m}}/\mathrm{J\,K^{-1}\,mol^{-1}} = 943.670 + 41.524X + 4.683X^2 + 29.970X^3 - 1.203X^4 - 53.554X^5 \tag{5}$$

where $X = (T/\mathrm{K}—384)/16$. This equation is valid between $T = 384$ and 400 K. The correlation coefficient for the fitting R^2 is 0.99954. The relative deviations of the smoothed heat-capacities obtained by the above equation from experimental heat-capacities are within ±0.1%.

Molar enthalpy and entropy of phase transition

Three series of the experiments in the region of the phase transition of the compound are carried out so that the reversibility and repeatability of the phase transition are verified. The results of three series of heat-capacity measurements are ploted in the inset of Fig. 3. It may be seen from the inset that there are some slight differences in heights and widths of the peaks corresponding to each series of heat-capacity measurements during phase transition of the sample. However, the phase transition basically exhibits good reversibility and repeatability. A close agreement in C_P values of each series of repeated experiment is derived. The molar enthalpy $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ of the phase transition in $C_{p,\mathrm{m}}$–T curve is obtained from Eq. 6. The molar entropy $\Delta_{\mathrm{trs}}S_{\mathrm{m}}$ is calculated with the Eq. 7 [9, 10]

$$\Delta_{\mathrm{trs}}H_{\mathrm{m}} = \left[Q - n\cdot\int_{T_{\mathrm{i}}}^{T_{\mathrm{trs}}} C_{P(\mathrm{i})}\mathrm{d}T - n\cdot\int_{T_{\mathrm{trs}}}^{T_{\mathrm{f}}} C_{P(\mathrm{f})}\mathrm{d}T - \int_{T_{\mathrm{i}}}^{T_{\mathrm{f}}} H_0\mathrm{d}T\right]\Big/ n \ \left(\mathrm{kJ\,mol^{-1}}\right) \qquad (6)$$

$$\Delta_{\mathrm{trs}}S_{\mathrm{m}} = \Delta_{\mathrm{trs}}H_{\mathrm{m}}/T_{\mathrm{trs}} \ \left(\mathrm{J\,mol^{-1}\,K^{-1}}\right) \qquad (7)$$

where T_{i} is the temperature slightly smaller than the starting temperature of the phase transition, T_{f} is the temperature slightly higher than the finishing temperature of the transition, $C_{P(\mathrm{i})}$ is the heat-capacity at the temperature T_{i}, $C_{P(\mathrm{f})}$ is the heat-capacity at the temperature T_{f}, Q is the total heat quantity introduced to the calorimeter from

Table 4 Experimental molar heat-capacities of the compound $(C_{11}H_{18}NO)_2CuCl_4(s)$ $\left[M_{(C_{11}H_{18}NO)_2CuCl_4} = 565.87\,\mathrm{g\,mol^{-1}}\right]$

T/K	$C_{p,\mathrm{m}}$/(J K^{-1} mol^{-1})	T/K	$C_{p,\mathrm{m}}$/(J K^{-1} mol^{-1})	T/K	$C_{p,\mathrm{m}}$/(J K^{-1} mol^{-1})
77.845	190.21	183.052	423.91	294.337	665.68
79.949	199.31	186.115	430.61	297.349	677.15
82.053	206.98	189.178	436.60	300.419	691.57
84.908	214.40	192.241	443.19	303.490	710.97
87.613	223.50	195.304	449.17	306.560	729.82
90.468	231.64	198.513	455.52	309.923	750.89
93.208	238.69	202.305	462.82	312.993	774.18
96.178	247.44	206.026	470.61	316.063	799.68
98.926	255.00	209.032	476.84	319.280	825.18
102.790	264.68	212.077	483.29	322.569	856.78
106.847	274.50	215.286	489.52	325.640	891.16
109.702	282.16	218.349	495.15	329.002	958.80
112.558	288.63	221.354	502.22	331.928	1050.3
115.413	294.62	224.359	508.69	335.299	1196.3
118.440	301.07	227.365	516.35	338.398	1427.8
121.357	306.28	230.671	522.82	341.389	1735.6
124.274	312.68	233.977	530.48	344.705	2217.8
127.191	319.03	236.982	537.66	347.750	2982.3
130.254	324.90	240.080	544.00	350.903	3956.2
133.171	330.88	243.873	551.11	353.296	4999.9
136.088	337.35	247.373	558.90	354.808	5884.8
139.005	342.14	250.582	565.96	356.224	1437.1
142.068	349.08	253.790	572.31	360.144	889.50
144.985	354.59	256.853	577.93	363.726	894.48
148.048	360.10	259.770	583.68	367.235	905.02
151.840	366.44	262.864	590.69	371.329	915.00
155.632	373.50	265.896	597.69	375.576	921.08
158.695	379.85	268.959	605.23	379.662	931.63
161.612	385.60	272.131	612.50	383.307	942.31
164.667	390.60	275.394	619.70	387.253	952.91
167.738	397.21	278.439	627.50	390.409	961.57
170.801	402.00	281.794	635.26	393.698	973.21
173.829	408.84	284.857	642.34	396.695	977.09
176.927	413.73	288.066	650.12		
179.844	418.16	291.128	657.90		

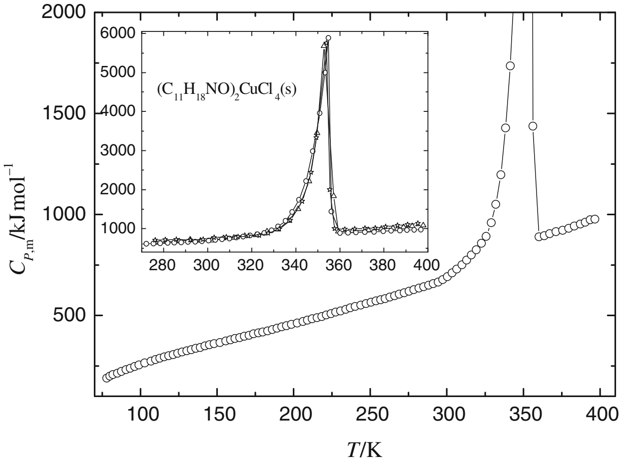

Fig. 3 Experimental molar heat-capacity curve of the complex $(C_{11}H_{18}NO)_2CuCl_4(s)$ with the temperature (K). In which "*open circle*", "*open triangle*", and "*open star*" represents the first, the second, and the third series of heat-capacity measurements, respectively

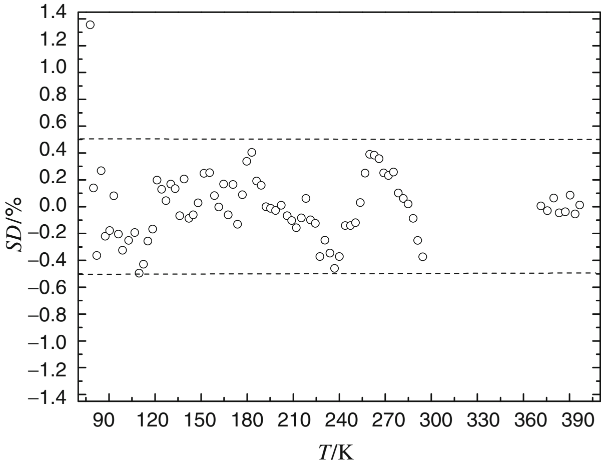

Fig. 4 The plot of the standard deviation of heat-capacity of $(C_{11}H_{18}NO)_2CuCl_4(s)$ against the absolute temperature, *SD*/%=$[(C_{smo} - C_{exp})/C_{exp}] \times 100\%$, C_{smo} and C_{exp} represent the smoothed and experimental molar heat-capacities of the compound before and after the solid–solid phase transition, respectively

temperature T_i to T_f, T_{trs} is the peak temperature of the phase transition of the sample, n is the mole number of the sample, H_0 is the heat-capacity of the empty sample cell. Values of Q and H_0 are calculated with the program stored in the computer linked with the adiabatic calorimetric system, and printed along with experimental results of heat-capacities.

The results of T_{trs}, $\Delta_{trs}H_m$, and $\Delta_{trs}S_m$ obtained from three series of repeated heat-capacity measurements are shown in Table 5.

Owing to the large enthalpy of the solid–solid phase transition, it may be used as a kind of thermal storage material.

Table 5 The results of the solid–solid phase transition of the compound obtained from three series of repeated heat-capacity measurements

Thermodynamic properties	T_{trs}/K	$\Delta_{trs}H_m$/ (kJ mol^{-1})	$\Delta_{trs}S_m$/ (J K^{-1} mol^{-1})
Series 1, x_1	354.808	76.227	51.668
Series 2, x_2	353.871	75.814	51.159
Series 3, x_3	353.963	76.939	51.194
Mean value, $(\bar{x} \pm \sigma_a)$	(354.214 ± 0.298)	(76.327 ± 0.328)	(51.340 ± 0.164)

$\sigma_a = \sqrt{\frac{\sum_{i=1}^{n}(x_i-\bar{x})^2}{n(n-1)}}$, in which n is experimental number ($n = 3$); x_1, experimental value of each series of repeated measurement; $\bar{x}$, mean value

Conclusions

Crystal structure and some thermodynamic parameters of the solid–solid phase transition of the complex were reported. The title compound can not only be used as a drug, but also as a thermal energy storage material.

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