Synthesis, Crystal Structure and Thermodynamic Properties of the Compound $(C_{10}H_{16}NO)_2CdCl_4 \cdot C_{10}H_{16}NOCl \cdot H_2O(s)$

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(Received on 2nd December 2009, accepted in revised form 20th September 2010)

Summary: A novel complex $(C_{10}H_{16}NO)_2CdCl_4 \cdot C_{10}H_{16}NOCl \cdot H_2O(s)$ was synthesized by the method of liquid phase reflux synthesis. FTIR, chemical and elemental analysis, and X-ray crystallography were applied to characterize the crystal structure and composition of the complex. The crystal structure of the complex belongs to triclinic system with space group $P\bar{1}$ and cell parameters a=0.55703(6) nm, b=1.39937(15) nm, c=1.40559(16) nm; α=117.819(2)°, β=98.8510(10)°, γ =96.5770(10)°, respectively. The compound is a salt, which consists of three $[C_{10}H_{16}NO]^+$ cations, a $[CdCl_4]^{2-}$ anion, a Cl^- anion and a water molecule. On account of electrostatic attraction and four types of intramolecular hydrogen bonds an infinite network supermolecule is formed. Low-temperature heat capacities of the compound were measured by a precise automated adiabatic calorimeter over the temperature range from 78 to 365 K. A polynomial equation of heat capacities against the temperature in the region of (78—365) K was fitted by least square method. Based on the fitted polynomial equation, the smoothed heat capacities and thermodynamic functions of the compound relative to the standard reference temperature 298.15 K were calculated at intervals of 5 K.

Introduction

Ephedrine hydrochloride is not only an important drug, but also one of main ingredients of many pharmaceutical prescription, which has an important pharmic value because of its higher biological activity. It can directly activate α or β adrenergic receptor, stretch bronchus and contract partial vas in a long time [1]. It also can suscitate the central nervous system and the heart, relax bronchial smooth muscle, contract bronchial mucosa and lung capillaries, reduce the hypoxia in body and adjust the blood pressure. Consequently, it shows a significant clinical effectiveness in the treatment of bronchial asthma, spinal anesthesia, nasal congestion, hypopiesia induced by epidural anesthesia, edema and other diseases [2], but it is still toxic to our body if taking in the long term because of its addiction. The coordination of cadmium with some biologically active small molecules can facilitate the removal of cadmium from the body and can decrease the accumulation of the element in the human body [3]. Therefor it has an important value to study this kind of compound. Study of the thermal stability of the drug are of great practical significance for the evaluation of storage period and quality control of drug production. In this paper, using ephedrine hydrochloride, cadmium chloride and hydrochloric acid as reagents, the title complex was synthesized. The crystal structure of the compound was characterized by X-ray crystallography, molar heat capacity was measured by using a precision small sample automated adiabatic calorimenter over the temperature range of (78 to 365) K, the experimental values of the heat capacities were fitted by least squares method. The smooth heat capacities and thermodynamic functions relative to 298.15 K have been calculated based on the fitted polynomial equation [4-6].

Results and Discussion

The molecular structure of title compound was shown in Fig.1, in which the asymmetric unit consists of three $[C_{10}H_{16}NO]^+$ cations, one $[CdCl_4]^{2-}$ anion, one Cl^- anion, and one crystallization water molecule, and the molecular formula can be determined as $(C_{10}H_{16}NO)_2CdCl_4 \cdot C_{10}H_{16}NOCl \cdot H_2O$.

The compound is clearly different from the previous described as $(C_{10}H_{16}NO)$ $[CdCl_3H_2O]$ (N.G.Charles *et al.*, 1984) [7]

In the title compound, one imino proton is offered by nitrogen atom in each ephedrine, which forms univalent cation. It is interesting that cadmium atom does not participate in coordinating with ni-

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trogen or oxygen atom of ephedrine ligands, which have coordinated ability, but coordinates with four chlorine atoms (the other is a dissociative chlorine atom), and forms a slightly distorted triangular pyramid.

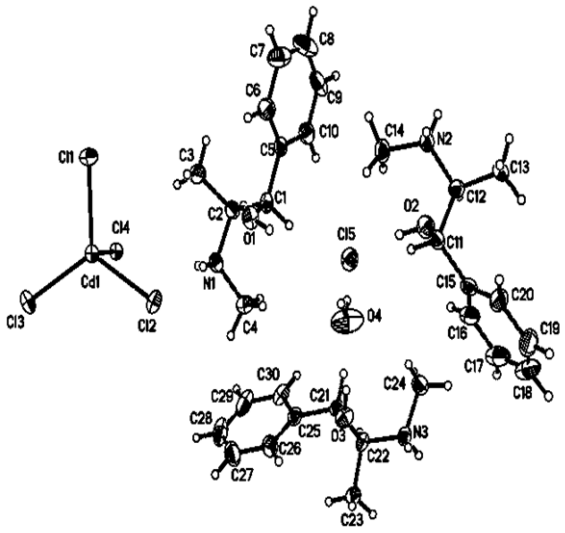

Fig.1: The molecular structure diagram of title compound.

The bond length of Cd(1)-Cl(4) was longer than the bond length of Cd(1)-Cl(1), Cd(1)-Cl(2) and Cd(1)-Cl(3) obviously (see Table-4), so Cl(4) is located at the top of triangular pyramid. The bond angles of Cl(1)-Cd(1)-Cl(3), Cl(2)-Cd(1)-Cl(3), and Cl(2)-Cd(1)-Cl(1) are 118.81(5)°, 119.45(6)°, and 119.52(6)° respectively, videlicet the total of three bond angles is 357.78°, which is close to 360°, namely Cd(1), Cl(1), Cl(2), and Cl(3) are almost located in a same plane, and the three bond angles approach 120° respectively, which suggests that Cd(1) is almost located in symmetry-center of the plane. The bond angles of Cl(2)-Cd(1)-Cl(4), Cl(2)-Cd(1)-Cl(4)#1, Cl(3)-Cd(1)-Cl(4), Cl(1)-Cd(1)-Cl(4), and Cl(1)-Cd(1)-Cl(4)#1 are 95.08(5)°, 95.69(5)°, 85.17(5)°, 84.93(5)°, and 94.11(5)° respectively, which means it is not a right triangular pyramid. Triangular pyramids invert along the Cd(1)-Cl(4) axis in space, form an infinite one-dimensional straight chain, and stack up. $[CdCl_4]^{2-}$ anion bonds with the others unit through electrostatic attraction and hydrogen bonds to form a stable molecule. The water molecules were dispersed in their interspaces and several hydrogen bonds are formed (summarized in Table-1).

Table-1: Hydrogen bond lengths(nm) and bond angles(°) for title complex*

D-H...A	d(D-H)	d(H...A)	d(D...A)	□(DHA)
O(4)-H(4G)...Cl(5)#1	0.085	0.232	0.3160(7)	170.5
O(4)-H(4F)...Cl(5)	0.085	0.235	0.3192(7)	170.5
N(3)-H(3B)...Cl(4)#3	0.090	0.284	0.3527(5)	134.5
N(3)-H(3B)...Cl(1)#4	0.090	0.252	0.3260(5)	139.5
N(3)-H(3A)...Cl(1)#3	0.090	0.236	0.3221(5)	159.4
O(3)-H(3)...O(4)	0.082	0.191	0.2722(8)	172.0
N(2)-H(2B)...Cl(4)#5	0.090	0.275	0.3475(5)	138.3
N(2)-H(2B)...Cl(3)#6	0.090	0.255	0.3247(5)	134.7
N(2)-H(2A)...Cl(3)#5	0.090	0.236	0.3206(6)	156.1
O(2)-H(2)...Cl(5)#1	0.082	0.243	0.3219(5)	160.7
N(1)-H(1B)...Cl(2)#2	0.090	0.253	0.3255(5)	138.3
N(1)-H(1B)...Cl(4)	0.090	0.284	0.3541(5)	136.2
N(1)-H(1A)...Cl(2)	0.090	0.236	0.3215(5)	158.0
O(1)-H(1)...Cl(5)#1	0.082	0.243	0.3252(5)	176.6

* Symmetry transformations used to generate equivalent atoms: #1 x+1, y, z; #2 x-1, y, z; #3 x, y, z+1; #4 x-1, y, z+1; #5 x, y-1, z ; #6 x-1, y-1, z

There are four types of intramolecular hydrogen bonds in the title compound [8]. One hydrogen bond is (N-H··Cl) between the nitrogen atom of imino group of the cation and the chlorine atom of cadmium tetrachloride anion. The other hydrogen bond is (O-H···Cl), which occurs between the oxygen atom of a water molecule and the dissociative chlorine anion including O(4)-H(4G)···Cl(5)#1 and O(4)-H(4F)···Cl(5). The third, O(3)-H(3)···O(4), occurs between oxygen atom of hydroxyl group of one $[C_{10}H_{16}NO]^+$ cation and oxygen atom of a water molecule. The fourth, occurs between oxygen atoms of hydroxyl groups of other two $[C_{10}H_{16}NO]^+$ cations except which the third kind of hydrogen bond was refered and the chlorine atom of the anion was dissociated including O(2)-H(2)···Cl(5)#1 and O(1)-H(1)···Cl(5)#1. Thanks to all of above referring hydrogen bonds, an infinite twelve-member-loop spatial network with the alternate appearance of $[C_{10}H_{16}NO]$- $[CdCl_4]$ and $[C_{10}H_{16}NO]$- [Cl]-H_2O was formed, and the extended supramolecular structure and the network diagram was displayed in Fig. 2 as well as the packing diagram was presented in Fig. 3. The results indicate that the electrostatic attration and hydrogen bonds play an important role in enhancing the robustness of the whole structure.

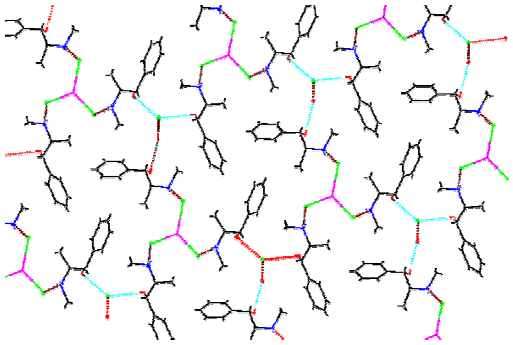

Fig. 2: The infinite twelve-member-loop spatial network formed through hydrogen bonds between adjacent chains of title compound viewing along a-axis.

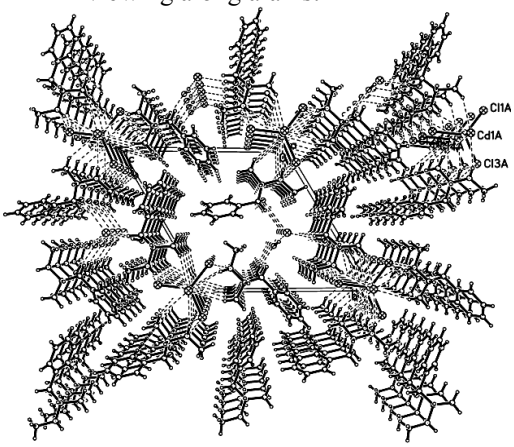

Fig. 3: The crystallographic packing diagram of title compound.

The experimental molar heat capacities were presented in Fig. 4, which show that molar heat capacities smoothly go up with the increasing temperature, and the structure of the complex is stable over the temperature range between T = 78 K and T = 365 K, no phase change, association nor thermal decomposition occurred. A polynomial equation of the experimental molar heat capacities ($C_{p,m}$) against reduced temperatures (X), $X = f(T)$, was fitted by least-squares method in the temperature regions of (78 to 365) K:

$$C_{p,m}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) = 760.551+485.064X+73.037X^2 -39.999X^3-51.380X^4+39.384X^5 \quad (1)$$

in which $X=(T-221.5)/143.5$ [9]. This equation is valid over the temperature range from 78 to 365 K. The correlation coefficient for the fitting R^2= 0.99997 with an uncertainty ±0.20 %.

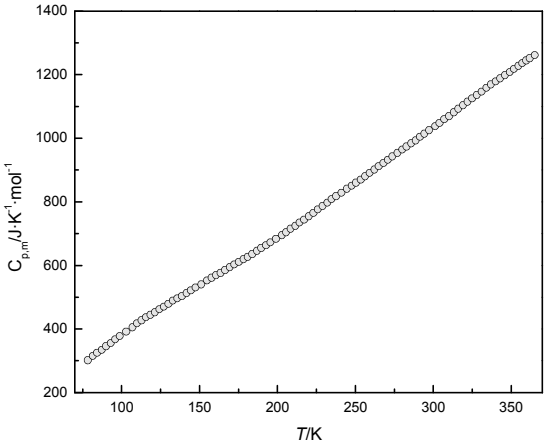

Fig. 4: Experimental molar heat capacities of the title complex.

The smoothed molar heat capacities and thermodynamic functions of the title complex were calculated based on the fitted polynomial equation of heat capacities against the reduced temperature (X) according to the following thermodynamic equations:

$$(H_T-H_{298.15})= \int_{298.15}^{T} C_{p,\mathrm{m}}\cdot \mathrm{d}T \quad (2)$$

$$(S_T-S_{298.15})= \int_{298.15}^{T} C_{p,\mathrm{m}}\cdot T^{-1}\mathrm{d}T \quad (3)$$

The smoothed heat capacities and thermodynamic functions of the compound relative to the standard reference temperature 298.15 K were tabulated in Table-2 at intervals of 5 K.

Experiment

All chemicals, ephedrine hydrochloride, $CdCl_2\cdot 2.5H_2O$, hydrochloric acid and anhydrous ethanol used in the experiments were of analytical grade (produced by Tianjin Third Reagent Factory). Strictly according to the molar ratio (3: 1: 2), appropriate amount of ephedrine hydrochloride, hydrated cadmium chloride and hydrochloric acid were weighed based on stoichiometric coefficients of the reaction. The mixture of ephedrine hydrochloride and cadmium chloride were put into agate mortar and ground. Then the mixture was dissolved in anhydrous ethanol in a big beaker, hydrochloric acid was slowly added and stirred evenly, then the mixed solution refluxed about 10 hours.

Table-2: Smoothed heat capacities and thermodynamic functions of title complex

T /(K)	$C_{p,m}$ /(J·K^{-1}·mol^{-1})	H_T-$H_{298.15}$ /(kJ·mol^{-1})	S_T-$S_{298.15}$ /(J·K^{-1}·mol^{-1})
80	306.29	-144.56	-773.96
85	326.83	-142.97	-754.76
90	346.32	-141.29	-735.54
95	364.90	-139.51	-716.34
100	382.68	-137.64	-697.19
105	399.77	-135.69	-678.12
110	416.27	-133.65	-659.15
115	432.27	-131.53	-640.29
120	447.87	-129.33	-621.55
125	463.13	-127.05	-602.95
130	478.14	-124.70	-584.48
135	492.96	-122.27	-566.14
140	507.64	-119.77	-547.93
145	522.25	-117.19	-529.85
150	536.84	-114.54	-511.89
155	551.43	-111.82	-494.05
160	566.09	-109.03	-476.31
165	580.83	-106.16	-458.67
170	595.68	-103.22	-441.12
175	610.67	-100.20	-423.64
180	625.82	-97.114	-406.24
185	641.15	-93.946	-388.89
190	656.66	-90.702	-371.60
195	672.36	-87.380	-354.35
200	688.26	-83.978	-337.14
205	704.36	-80.497	-319.95
210	720.66	-76.934	-302.79
215	737.15	-73.290	-285.64
220	753.83	-69.562	-268.50
225	770.69	-65.751	-251.37
230	787.72	-61.855	-234.24
235	804.90	-57.874	-217.11
240	822.24	-53.806	-199.97
245	839.70	-49.651	-182.83
250	857.27	-45.409	-165.68
255	874.95	-41.078	-148.52
260	892.71	-36.659	-131.35
265	910.53	-32.151	-114.17
270	928.40	-27.554	-96.975
275	946.30	-22.867	-79.774
280	964.22	-18.091	-62.562
285	982.15	-13.225	-45.340
290	1000.1	-8.2692	-28.108
295	1017.9	-3.2242	-10.867
298.15	1029.2	0	0
300	1035.8	1.9101	6.3836
305	1053.6	7.1335	23.643
310	1071.3	12.446	40.910
315	1089.0	17.847	58.186
320	1106.6	23.336	75.469
325	1124.2	28.913	92.760
330	1141.6	34.577	110.06
335	1159.1	40.329	127.36
340	1176.5	46.168	144.67
345	1193.8	52.094	161.98
350	1211.1	58.107	179.30
355	1228.4	64.206	196.61
360	1245.8	70.391	213.92
365	1263.2	76.664	231.22

The final solution was naturally cooled to room temperature, and laid silently. Several days later, a colourless crystal suitable for X-ray analysis was obtained. Chemical and elemental analysis (model: PE-2400, Perkin Elmer, USA) have shown that practical contents of C, H, N, O, Cd and Cl in the compound have been measured to be 54.25 %, 7.55 %, 6.33 %, 9.63 %, 16.92 % and 5.32 %. Theoretical contents of C, H, N, O, Cd and Cl in the compound have been calculated to be 54.22 %, 7.58 %, 6.32 %, 9.63 %, 16.91 % and 5.34 % respectively. This showed the purity of the sample prepared was higher than 99.50 %.

A suitable single crystal of the complex was glued to a fine glass fiber and was then mounted on Bruker Smart-1000 CCD diffractometer with MoKα radiation (λ= 0.071073 nm). The intensity data were collected in the ω–2θ scan mode at 298(2) K. The empirical absorption corrections were based on multi-scan. The structure was solved by direct method and expanded using Fourier techniques with SHELXL-97 program [10] and all non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares methods using the SHELXT-97 program [10]. Crystal data as well as details of data collection and refinements for the complex were summarized in Table-3 and the selected bond distances and angles were listed in Table-4.

The heat capacities of the compound were measured by a precision automatic adiabatic calorimeter over the temperature range 78 ≤ (T/K) ≤ 365. The calorimeter was established in the Thermochemistry Laboratory of the College of Chemistry and Chemical Engineering, Liaocheng University, China. The principle and performance of the adiabatic calorimeter, and the procedures of heat capacity measurements have been described in detail elsewhere [11, 12].

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 to 0.4) K·min^{-1} and (1 to 3) K.

Table-3: Crystal data and structure refinement parameters for title compound.

Empirical formula	$C_{30}H_{50}CdCl_5N_3O_4$
Formula weight	806.38
Temperature/ K	298(2)
Wavelength/ nm	0.071073
Crystal system	Triclinic
Space group	P1
***a*/nm**	0.55703(6)
***b*/nm**	1.39937(15)
***c*/nm**	1.40559(16)
α/ (°)	117.819(2)
β/ (°)	98.8510(10)
γ/ (°)	96.5770(10)
Volume/ nm ^{3}	0.93546(18)
Z	1
Calculated density /(g·cm^{-3})	1.431
Absorption coefficient /mm^{-1}	0.977
***F*(000)**	416
Crystal size	0.48 mm x 0.43 mm x 0.40 mm
θ range for date collection/(°)	1.68 to 25.01
Limiting indices	-6≤h≤6, -16≤k≤16, -11≤l≤16
Reflections collected / unique	4842 / 3933 [*R*(int) = 0.0190]
Completeness to θ = 25.01	97.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6961 and 0.6514
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3933 / 3 / 389
Goodness-of-fit on F^2	1.071
Final R indices [*I*>2σ(I)]	*R1* = 0.0338, *wR2* = 0.0855
***R* indices (all data)**	*R1* = 0.0349, *wR2* = 0.0866
Absolute structure parameter	0.01(2)
Extinction coefficient	0.016(2)
Largest diff. peak and hole/(e·nm^{-3})	1024 and 967

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} to 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 [9].

Table-4: Selected bond lengths (nm) and bond angles (°) of title compound*

Cd(1)-Cl(2)	0.24558(14)	Cl(2)-Cd(1)-Cl(4)	95.08(5)
Cd(1)-Cl(1)	0.24570(14)	Cl(1)-Cd(1)-Cl(4)	95.69(5)
Cd(1)-Cl(3)	0.24595(13)	Cl(3)-Cd(1)-Cl(4)	94.11(5)
Cd(1)-Cl(4)	0.26475(16)	Cl(2)-Cd(1)-Cl(4)#1	84.93(5)
Cd(1)-Cl(4)#1	0.29230(16)	Cl(1)-Cd(1)-Cl(4)#1	85.17(5)
Cl(4)-Cd(1)#2	0.29230(16)	Cl(3)-Cd(1)-Cl(4)#1	85.02(5)
Cl(2)-Cd(1)-Cl(1)	118.81(5)	Cl(4)-Cd(1)-Cl(4)#1	179.00(7)
Cl(2)-Cd(1)-Cl(3)	119.45(6)	Cd(1)-Cl(4)-Cd(1)#2	179.00(7)
Cl(1)-Cd(1)-Cl(3)	119.52(6)		

* Symmetry transformations used to generate equivalent atoms: #1 x+1, y, z; #2 x-1, y, z

The performance of the adiabatic calorimeter had been confirmed by the measurment of the heat capacities of reference standard material (α-Al_2O_3) over the temperature range $77 \leq (T/\mathrm{K}) \leq 402$. The deviations of the experimental results from those of the smoothed curve lie within ± 0.20 %, while the uncertainty is ± 0.30 %, as compared with the values given by the former National Bureau of Standards over the whole temperature range [13].

The mass of the sample of title compound used in calorimetric measurements was 2.68283 g, which was equivalent to 0.0033 mol in terms of its molar mass, M = 806.38 g·mol^{-1}.

Conclusions

This paper mainly reported the crystal structure, the low temperature heat capacities, and thermodynamic properties of the title compound $(C_{10}H_{16}NO)_2CdCl_4 \cdot C_{10}H_{16}NOCl \cdot H_2O$ (s).

Acknowledgements

This work was financially supported by the National Science Foundations of China under the contract NSFC No. 20673050 and 20973089, and the Natural Science Foundation of Shaanxi Province (No. 2009JM2014).

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