Synthesis, crystal structure and thermochemistry of the coordination compound of pyridine-2,6-dicarboxylic acid with barium ion

Yu-Han Zhang [a], You-Ying Di [a,*], Zhi-Cheng Tan [b], Jian-Min Dou [a]

[a] *Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, Shandong Province, PR China*
[b] *Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China*

ABSTRACT

The complex of pyridine 2,6-dicarboxylate with Ba^{2+} ion $Ba(HDPC)_2 \cdot 2H_2O(s)$ was synthesized. X-ray crystallography was applied to characterize the crystal structure of the complex. Low-temperature heat capacities of the complex were measured with an automated adiabatic calorimeter in the temperature range from 78 to 360 K. A polynomial equation of experimental molar heat capacities as a function of the temperature was obtained by the least-squares method. The smoothed heat capacities and thermodynamic functions of the complex were calculated based on the fitted polynomial equation. In addition, the standard molar enthalpies of dissolution for the reactants and products of the synthesis reaction in a selected solvent were measured by an isoperibol solution-reaction calorimeter, and the standard molar enthalpy of formation of the title complex was calculated as $-(2993.0 \pm 3.0)\,kJ\,mol^{-1}$ by the Hess thermochemical cycle. Furthermore, the reliability of the designed thermochemical cycle was verified by UV–vis spectroscopy.

1. Introduction

Pyridine-2,6-dicarboxylic acid is an important chemical substance with obvious biological activity and has a wide application in medicine. Stereochemistry, structural chemistry, magnetism, spectroscopy, reaction dynamics and biochemical simulation system about its derivatives and complexes are deeply and widely studied. It is reported that the pyridine ring is more easily absorbed by organism and has less side effect than benzene ring. Accordingly, the design and synthesis of drugs with pyridine ring in pharmaceutical chemistry have attracted much attention [1].

Barium is a toxic metal and severely endangers health of humans and animals. Although barium ion is toxic, the stable coordination compounds of barium (Π) with many active organic molecules may reduce the toxicity of the barium ion, decrease the accumulation of the toxic metal in the biological body, and facilitate the removal of barium ion from the body.

In recent years, a great progress has been made for synthesis and characterization of structures and properties about the complexes of pyridine-2,6-dicarboxylic acid with metals [2,3]. But thermodynamic properties about these compounds are not found in the literatures. In this paper, Low-temperature heat capacities of the title complex are measured by a precise automated adiabatic calorimeter with a small sample. The results show that the heat capacity curves smoothly and slowly rise in the measured temperature range. The experimental heat capacities for the complex are fitted to a polynomial equation of experimental molar heat capacities vs. reduced temperature by the least-squares method. In addition, standard molar enthalpy of formation of the compound is investigated by an isoperibol solution-reaction calorimeter.

2. Experimental

2.1. Synthesis and characterization of the title complexes

Pyridine-2,6-dicarboxylic acid, and dihydrate barium chloride as reactants, and distilled water as the solvent are all of analytical grade. The reactants are accurately weighed at the molar ratio of $n(H_2DPC){:}n(BaCl_2 \cdot 2H_2O) = 2{:}1$, Pyridine-2,6-dicarboxylic acid is dissolved in the water beforehand. The resulting mixed solution is heated and concentrated with continuous stirring on the electric furnace for 2 h. 1 mol L^{-1} NaOH solution is added to adjust the pH of the mixture to 7.0, and it is heated for 8 h. Naturally cooled and filtered. The colorless needle crystals can be gained. After suction filtration, the crystals are recrystallized twice with double-deionized water. Finally, the product is dried in a vacuum oven,

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put in a weighing bottle, and preserved in a desiccator. Theoretical contents of H, C, N, O, and Ba in the compound have been calculated to be 2.39, 33.26, 5.54, 31.65, and 27.16% for Ba(HDPC)$_2$·2H$_2$O. Chemical and elemental analysis (model: PE-2400, Perkin Elmer, USA) have shown that the practical contents of the H, C, N, O, and Ba in the compound have been measured to be 2.41, 33.24, 5.53, 31.64, and 27.18%. This shows that the mass fraction purity of the sample prepared should be >0.9916.

2.2. X-ray crystallography

A suitable single crystal of the complex is glued to the fine glass fiber and then mounted on Bruker Smart-1000 CCD diffractometer with Mo Kα radiation (λ = 0.071073 nm). 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 structure is solved by direct method and difference Fourier synthesis, and all non-hydrogen atoms are refined anisotropically on F^2 by full-matrix least-squares method. All calculations are performed with the program package SHELXTL [4]. We have gotten the CCDC number for the compound Ba(HDPC)$_2$·2H$_2$O (NO: 929363).

2.3. Adiabatic calorimetry

A precise automatic adiabatic calorimeter is used to measure heat capacities in the temperature range from 78 to 360 K. The principle and structure of the adiabatic calorimeter are described in detail elsewhere [5]. Briefly, the calorimeter mainly comprises a sample cell, a platinum resistance thermometer, an electric heater, inner, middle and outer adiabatic shields, three sets of six junction-points of 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. The miniature platinum resistance thermometer (IPRT No. 2, produced by Shanghai Institute of Industrial Automatic Meters, 16 mm in length, 1.6 mm in diameter, and a nominal resistance of 100 Ω) is applied to measure the temperature of the sample. The thermometer is 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 are automatically recorded by use of a Data Acquisition/Switch Unit (Model 34970A, Agilent, USA) and processed online by a computer.

To verify the accuracy of the calorimeter, the heat capacities of the reference standard material (α-Al$_2$O$_3$) are measured in the temperature range from 78 to 400 K. The sample mass used is 1.7143 g, which is equivalent to 0.0168 mol based on its molar mass, M(Al$_2$O$_3$) = 101.9613 g mol^{-1}. Deviations of the experimental results from those of the smoothed curve lie within ±0.2%, while the uncertainty is ±0.3%, as compared with the values given by the former National Bureau of Standards in the whole temperature range [6].

Heat capacity measurements are 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 are generally controlled at 0.1–0.4 K min^{-1} and 1–3 K. The heating duration is 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period are always kept within ±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 of the Ba(HDPC)$_2$·2H$_2$O used for calorimetric measurement is 1.91376 g, which is equivalent to 0.0038 mol in terms of its molar mass, M = 505.6 g mol^{-1}.

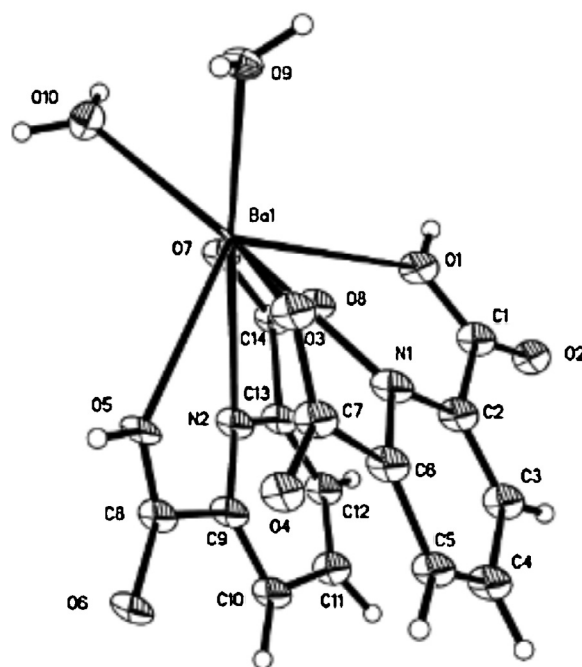**Fig. 1.** Structure of the title complex Ba(HDPC)$_2$·2H$_2$O(s).

2.4. Isoperibol solution-reaction calorimetry

The isoperibol solution-reaction calorimeter consists primarily of a precise temperature controlling system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silica glass, a precise temperature measuring system, and a data acquisition system. The principle and structure of the calorimeter are described in detail elsewhere [6].

The reliability of the calorimeter is verified previously [7] by measuring enthalpy of dissolution of KCl (calorimetrically primary standard) in double-distilled water. According to the molar ratio of KCl to H$_2$O, n(KCl):n(H$_2$O) ≈ 1:1110, the KCl is dissolved in 100 cm^3 of double-distilled water at T = (298.15 ± 0.001) K. The mean enthalpy of dissolution is (17,597 ± 13) J mol^{-1} for KCl, which compares with corresponding published data (17,536 ± 3.4) J mol^{-1}, under the same experimental conditions [7].

In all dissolution experiments of the sample, reasonable reagent (1 mol dm^{-3} of hydrochloric acid) is chosen as the calorimetric solvent. Finally, the results of UV/V are used to confirm whether the designed thermochemical cycle is reasonable or not. These results have indicated that chemical components and physicochemical properties of initial solution are consistent with those of the reacted solutions.

3. Results and discussion

3.1. Description of crystal structure of the complex

The molecular structure of the complex is shown in Fig. 1. The space crystal packing of the complex is shown in Fig. 2. The crystal data and refinement detail are summarized in Table 1. The selected bond lengths and angles of the title complex are listed in Table 2.

In the crystal structure of Ba(HDPC)$_2$·2H$_2$O, both ligand molecules of the compound provide two oxygen atoms (O1, O3, O5 and O7) and an N atom (N1, N2). Barium ion and two pyridine rings are not on the same plane. The angle between pyridine ring and Ba—N bond is about 32°. The average bond length of Ba1—N is 2.86 Å, The average bond length of Ba1—O is 2.82 Å, the average