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Synthesis, structural characterization and thermochemistry of copper pyridine 2,6-dicarboxylate trihydrate

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ABSTRACT

Copper pyridine 2,6-dicarboxylate trihydrate ($Cu(H_2DPC)(DPC)\cdot 3H_2O$) was synthesized. X-ray crystallography, chemical analysis, and elemental analysis were applied to characterize the structure and composition of the complex. Low-temperature heat capacities of the complex were measured with a small sample automated adiabatic calorimeter. The smoothed molar heat capacities and thermodynamic functions of the complex relative to the standard reference temperature 298.15 K were calculated based on the fitted polynomial equation. A reasonable thermochemical cycle was designed, and 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. Eventually, the standard molar enthalpy of formation of the title complex was calculated as $-(2389.92 \pm 2.53)$ kJ mol^{-1} by the Hess thermochemical cycle. In addition, the reliability of the designed thermochemical cycle was verified by UV–vis spectroscopy.

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1. Introduction

Pyridine-2,6-dicarboxylic acid (abbreviated as H_2DPC) has the wonderful biological activities and plays an important role in the field of medicine. In the past few years, much attention have been paid to the metal complexes involving pyridine-2,6-dicarboxylic acid [1,2] because it is found that the pyridine ring is more absorbable and has less side-effects than benzene ring. Therefore the preparation and application of pyridine heterocyclic drugs receive much attention. Because of the prominent activity of this complex, the potential therapeutics for some cancers and synthesizing new anticancer drugs will be turned into reality. In addition, it is well-known that the copper is one of the trace elements necessary for the health of humans, animals, and plants. It is closely related to more than 30 kinds of enzymes in the human body to promote growth and development of tissues. Diminishing copper content in the human body may result in many kinds of diseases, including sugar diabetes, cardiovascular diseases, and so on [3].

The standard molar enthalpy of formation of a substance is one of the important pieces of information required when calculating enthalpy changes, equilibrium constants, and theoretical yields of reactions. However, up to now, the synthesis, crystal structure, and standard molar enthalpy of formation of the title complex have not been reported in the literature. These results are needed in order to develop its new applications, to improve the techniques of chemical synthesis in which the complex participates, and to carry out relevant theoretical research [4]. In the present work, the crystal structure of the title complex ($Cu(H_2DPC)(DPC)\cdot 3H_2O$), the low-temperature heat capacities, and the enthalpies of dissolution of reactants and products of the liquid phase reaction in the chosen solvent are measured. Eventually, enthalpy change of the synthesis reaction and standard molar enthalpy of formation of the product $Cu(H_2DPC)(DPC)\cdot 3H_2O(s)$ are derived from the above experimental results.

2. Experimental

2.1. Synthesis and characterization of the sample

The pyridine-2,6-dicarboxylic acid and cupric chloride dihydrate as the reactants are all of analytical grade with a labeled purity of more than 99.5% and accurately weighed at the molar ratio of $n(H_2DPC):n(CuCl_2\cdot 2H_2O) = 4:1$. The two reactants are dissolved in anhydrous ethanol, separately. Then the solution of $CuCl_2\cdot 2H_2O$ is added to the solution of H_2DPC under sufficient stirring. The crude product is washed three times by anhydrous ethanol (A.R.) and recrystallized three times by anhydrous ethanol. Blue single

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crystals suitable for X-ray diffraction are obtained one week later by slow evaporation of the mixed solution. Finally, the sample is placed in a vacuum desiccator to dry at ambient temperature for 6 h.

Theoretical contents of H, C, N, O, and Cu in the compound have been calculated to be 3.14, 37.38, 6.23, 39.13, and 14.13%, respectively. Chemical analysis and element analysis (model: PE-2400, Perkin Elmer, USA) have shown that the practical contents of H, C, N, O, and Cu in the compound have been measured to be 3.13, 37.40, 6.25, 39.09, and 14.14%, respectively. This shows that the mass fraction purity of the sample prepared is higher than 0.9968.

2.2. X-ray crystallography

A single crystal suitable for X-ray analysis is glued to a fine glass fiber and mounted on the Bruker Smart-1000 CCD diffractometer with Mo-Kα radiation, $\lambda = 0.71073$ Å. A criterion of observability is used for the solution and refinement. The intensity data are collected at $T = 298.2$ K. The structure is solved by direct methods and expanded using Fourier techniques with SHELXL-97 program [5]. The non-hydrogen atoms are refined anisotropically by full-matrix least-squares calculations on F^2. The hydrogen atoms are located theoretically, riding on the concerned atoms and not refined.

2.3. Adiabatic calorimetry

A precise automatic adiabatic calorimeter is used to measure heat capacities over the temperature range from 78 to 384 K. The calorimeter is established in the Thermochemistry Laboratory of the College of Chemistry and Chemical Engineering, Liaocheng University, China. The principle and structure of the adiabatic calorimeter are described in detail elsewhere [6]. 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_2O_3) are measured over the temperature range from 78 to 400 K. The sample mass used is 1.71430 g, which is equivalent to 0.016813 mol based on its molar mass, $M(Al_2O_3) = 101.9613$ 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 over the whole temperature range [7].

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 $\pm 10^{-4}$ 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 [5]. The sample mass used for calorimetric measurements is 1.97610 g, which is equivalent to 0.0043932 mol in terms of its molar mass, $M = 449.81$ g mol^{-1}.

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 silicate glass, a precise temperature measuring system, and a data acquisition system. The main parameters of the isoperibol solution-reaction calorimeter are described in the literature [8]. The effective volume of Dewar flask is 100 cm^3. Measuring unit is made up of Dewar flask, sample cell, thermistor used for temperature measuring, small stirrer, and electric heater. The resistance of thermistor is varied with temperature, and temperature resolution is ±0.0001 K. The controlling precision of thermostatic water bath is $\pm 1 \times 10^{-3}$ K. The principle and structure of the calorimeter are described in detail elsewhere [8,9].

The reliability of the calorimeter is verified previously [9] by measuring enthalpy of dissolution of KCl (calorimetrically primary standard) in double-distilled water. According to the molar ratio of KCl to H_2O, $n(\mathrm{KCl}):n(\mathrm{H_2O}) \approx 1:1110$, the KCl is dissolved in 100 cm^3 of double-distilled water at $T = (298.15 \pm 0.001)$ K. The mean enthalpy of dissolution is (17597 ± 13) J mol^{-1} for KCl, which compares with corresponding published data, (17536 ± 3.4) J mol^{-1}, under the same experimental conditions [10]. The uncertainty of the calorimeter is calculated by comparison of our measured value with that of NIST from the enthalpy of dissolution of KCl in water to be ±0.3%.

In all dissolution experiments of the sample, 100 cm^3 of hydrochloric acid (HCl) with 0.1 mol dm^{-3} of concentration is chosen as the calorimetric solvent. Finally, the results of UV–vis and the data of the refractive indexes 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. Crystal structure of $Cu(H_2DPC)(DPC)\cdot 3H_2O(s)$

The molecular structure of $Cu(H_2DPC)(DPC)\cdot 3H_2O(s)$ is shown in Fig. 1. The crystal data and refinement details are summarized in Table 1. The selected bond lengths and angles of the title complex are listed in Table 2. Unit cell parameters are $a = 13.4180(15)$ Å, $b = 10.3266(12)$ Å, $c = 13.8029(18)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 114.2820(10)^\circ$, respectively. The crystal system of the coordination compound is monoclinic, and the space group is *P*c. The structure of the title compound includes two ligand molecules. One of them is neutral molecule and another is bivalent anion. The nitrogen atom (Cu1–N1 = 1.916(5) Å) from bivalent anion and two carboxyl oxygen (Cu1–O1 = 2.049(5) Å, Cu1–O3 = 2.019(5) Å) with negative charge as ligands coordinate with copper atom. And the copper ion also coordinate with the nitrogen atom (Cu1–N2 = 2.004(5) Å) from neutral molecule and two free carboxyl oxygen atoms (Cu1–O5 = 2.313(5) Å, Cu1–O7 = 2.468(5) Å). The data of torsion angles N(1)–C(6)–C(7)–O(3) = 3.6(8)° and N(2)–C(13)–C(14)–O(7) = –2.5(9)° shows that the carboxyl anion and carboxyl group are nearly planar with pyridine rings. Coordination polyhedron of copper ion is distorted octahedron. According to the data of bond length we can see that the binding ability of copper

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