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Synthesis, crystal structure and thermochemistry of nickel hydrogen pyridine-2,6-dicarboxylate

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ABSTRACT

Nickel hydrogen pyridine-2,6-dicarboxylate trihydrate ($Ni(HDPC)_2{\cdot}3H_2O$) was synthesized by the method of liquid phase synthesis. The composition and crystal structure of the complex were determined by chemical analysis, elemental analysis, and X-ray crystallography. Low-temperature heat capacities of the complex were measured over the temperature range from 78 to 353 K. 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. Eventually, the standard molar enthalpy of formation of the title complex was derived to be $-(2467.9 \pm 3.2)\,kJ\,mol^{-1}$ in accordance with Hess's law.

1. Introduction

Pyridine-2,6-dicarboxylic acid (abbreviated as H_2DPC) has excellent pharmacologic 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] since it is found that the pyridine ring is more absorbable and has less side-effects than benzene ring. Therefore the application and preparation of pyridine heterocyclic drugs have received much attention. And the studies have shown that three Ga(III)-complexes involving H_2DPC have significant inhibiting effect on gram-positive pathogens, which helps to probe the potential therapeutics for some cancers and to synthesize new anticancer drugs. Pyridine-2,6-dicarboxylic acid possesses diverse functional groups and has the ability to build stabilizing structures with divalent metals. Therefore, systematic studies on the synthesis, crystal structure and some properties of such complexes could enrich the basic theoretical knowledge of coordination chemistry.

The crystal structure and some important thermodynamic properties of the title compound, e.g., low-temperature heat capacities and standard molar enthalpy of formation, have not been found in the literature, which restricts the progress of relevant theoretical studies and application development of the compound. The heat capacity and standard molar enthalpy of formation of a substance are some of the fundamental thermodynamic properties and closely related to other physical, biological, physiological, and chemical properties [2,3]. In the present work, crystal structure of the title complex ($Ni(HDPC)_2{\cdot}3H_2O$) is determined by X-ray crystallography, low-temperature heat capacities are measured by a precise automated adiabatic calorimeter, molar enthalpies of dissolution of reactants and products of a designed thermochemical reaction are measured by isoperibol solution-reaction calorimetry. Thermodynamic functions and standard molar enthalpy of formation of the title compound are derived from these experimental results.

2. Experimental

2.1. Synthesis of crystalline $Ni(HDPC)_2{\cdot}3H_2O(s)$

Pyridine-2,6-dicarboxylic acid and nickel chloride hexahydrate used as the reactants are all of analytical grade with a labeled purity of more than 99.5%, and de-ionized water is used as the solvent in the synthesis reaction. 0.0005 mol of pyridine-2,6-dicarboxylic acid is weighted as the norm and nickel chloride hexahydrate is accurately weighed at molar ratio of $n(H_2DPC):n(NiCl_2{\cdot}6H_2O) = 1:1$. First, 0.0836 g of pyridine-2,6-dicarboxylic acid is dissolved in 100 cm^3 of de-ionized water. Then 0.1188 g of solid $NiCl_2{\cdot}6H_2O$ is added to the solution of H_2DPC under sufficient stirring. Finally, the concentrations of the two reactants in solvent are about

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0.005 mol dm^{-3}, respectively. After they are dissolved and mixed, the mixed solution is heated and refluxed for 11 h. The mixed solution is cooled at room temperature, the solid precipitation is separated out, and then the suction filtration and drying are carried out. The crude product is recrystallized three times by using the distilled water, and grass green acicular crystals suitable for X-ray diffraction are obtained. Finally, the sample is placed in a vacuum desiccator to dry in vacuum at ambient temperature for 6 h. Theoretical contents of H, C, N, O, and Ni in the compound have been calculated to be 3.17, 37.79, 6.30, 39.55, and 13.19%, respectively. Chemical analysis and element analysis (model: PE-2400, Perkin Elmer, USA) have shown that the practical contents of H, C, N, O, and Ni in the compound have been measured to be 3.19, 37.78, 6.31, 39.52, and 13.20%, respectively. This shows that the mass fraction purity of the sample prepared is higher than 0.9937.

2.2. X-ray crystallography

A crystal with dimensions of 0.48 mm × 0.37 mm × 0.36 mm is glued to a fine glass fiber and then mounted on the Bruker Smart 1000 CCD diffractometer with Mo-Kα radiation, λ = 0.71073 Å. The intensity data are collected at $T = 298 \pm 2$ K. The structure is solved by direct methods and expanded using Fourier technique with the SHELXL-97 program [4]. The non-hydrogen atoms are refined anisotropically by full-matrix least-squares calculations on F^2. The hydrogen atoms are added theoretically, ride 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 $T = 78$ K to $T = 353$ 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 [5,6]. 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 junctions 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 measuring precision of the miniature platinum resistance thermometer is ±0.001 K, the accuracy of measurement of calibration heat is ±0.299%, and the accuracy of voltage stability is ±0.004%. 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 $T = 78$ K to $T = 400$ K. The sample mass used is 1.7143 g, which is equivalent to 0.0168 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 ±0.29%, while the uncertainty is ±0.30%, 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. The sample mass used for calorimetric measurements is 1.98985 g, which is equivalent to 0.00447 mol in terms of its molar mass, $M = 444.96$ g mol^{-1}.

2.4. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG)

DSC and TG analyses are carried out in STA449C made by NETZSCH Corporation, Germany. The phase transition temperature and the latent heat are calibrated using high pure indium (purity: 99.999%) as a standard. The heating rate is 5 K min^{-1}. The material is protected by high purity nitrogen with a discharge rate of 40 cm^3 min^{-1}. The measurement on thermal analysis DSC/TG of the title compound is carried out under the same condition as above. The DSC/TG curves of the complex are measured by the use of amount of sample 11.5 mg.

2.5. Isoperibol solution-reaction calorimeter

The isoperibol solution-reaction calorimeter consists primarily of a precision temperature-controlling system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precision temperature measuring system, and a data acquisition system. The principle and structure of the calorimeter are described in detail elsewhere [8]. The precisions of controlling and measuring the temperature of the calorimeter can reach ±0.001 K and ±0.0001 K, respectively.

The reliability of the calorimeter is verified previously by measuring the enthalpy of dissolution of KCl (calorimetrically primary standard) in the double distilled water at $T = 298.15$ K. The mean enthalpy of dissolution is (17,597 ± 13) J mol^{-1} for KCl, which compares with the corresponding published data, (17,536 ± 3.4) J mol^{-1} under the same experimental condition [9]. The relative deviation of enthalpy of dissolution is within ±0.3%, and it is in the normal error range calorimetrically.

In all dissolution experiments of the sample, 100 cm^3 of 1% aqueous ammonia is chosen as the calorimetric solvent for measuring the enthalpies of dissolution of the reactants and products at $T = 298.15$ K. The tests have indicated that the volatility of aqueous solution of ammonia (1% NH_3) has no influence on experimental results. Finally, UV–vis spectra and the data of the refractive indexes are used to confirm whether the initial solution is in the same thermodynamic state as that of the reacted solution.

3. Results and discussion

3.1. Crystal structure

The molecular structure and packing of structure of $Ni(HDPC)_2 \cdot 3H_2O(s)$ are shown in Figs. 1 and 2, respectively. 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 $a = 13.6890(14)$ Å, $b = 10.0537(12)$ Å, $c = 13.7845(15)$ Å, $\alpha = \gamma = 90^\circ$, and $\beta = 115.1180(10)^\circ$, respectively. The crystal system of the coordination compound is