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Low-temperature heat capacity and the standard molar enthalpy of formation of compound chromium(III) tri(pyrazine-2-carboxylate)

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ABSTRACT

Low-temperature heat capacities of the coordination compound, chromium(III) tri(pyrazine-2-carboxylate), formulated as $Cr(pyza)_3$ (pyza = pyrazine-2-carboxylate), were measured by a precision automated adiabatic calorimeter over the temperature range of 78–400 K. A polynomial equation of heat capacities as a function of the temperature was fitted by the least square method. Based on the fitted polynomial equation, the fitted heat capacities and thermodynamic functions of the compound relative to the standard reference temperature 298.15 K were calculated at the interval of 5 K. In accordance with a reasonable thermochemical cycle designed, the standard molar enthalpy of formation of the title complex was determined to be -1207.86 ± 3.39 kJ mol^{-1} by an isoperibol solution–reaction calorimeter.

1. Introduction

The inorganic–organic hybrid materials has become a popular field of research in recent years due to the intriguing diversity of the structures and first for the usefulness in the areas like selective absorption, separation, gas storage, ion exchange, catalysis, optoelectronics and magnetic material [1–7]. In particular, rational selection of multifunctional ligands containing suitable coordination sites plays a crucial role in adjusting the network structure where the nature of the donor atoms may lead to the desired properties and functions. Multidentate N-/O-donor ligands are commonly used as organic spacers in the construction of coordination polymers. Pyrazine-2-carboxylic acid (Hpyza), a multifunctional heterocycle ligand with carboxylate group having three potential binding sites (one carboxylate group and two pyrazine-N atoms), has been frequently used for the construction of coordination polymers.

Only with thermodynamic data of substances can we quantitatively describe thermal stability and stable states at different temperatures and energy changing in different processes, and so on [8,9]. Since heat capacity is the fundamental quality from which other thermodynamic functions may be derived, it is clearly important to clarify the microstructure both theoretical and practical purposes from any apparently C_p behavior of compound. Extending our work [10], the coordination compound, chromium(III) tri(pyrazine-2-carboxylate), formulated as $Cr(pyza)_3$ (pyza = pyrazine-2-carboxylate), was synthesized in the present work, and structurally determined by X-ray crystallography. Low-temperature heat capacities of the title compound were measured by a precision automated adiabatic calorimeter over the temperature range from 80 to 390 K, and heat capacities and thermodynamic data were also obtained. In addition, the standard molar enthalpy of formation of the title complex was determined by an isoperibol solution–reaction calorimeter. We expect these results would facilitate the application of the title compound in the urgently needed fields.

2. Experimental

2.1. Materials and equipments

All reagents were of analytical grade and purchased commercially and used without further purification. The content of Cr^{3+} in $Cr(OH)_3 \cdot 3H_2O$ was complexometrially titrated, from which the mass fraction of $Cr(OH)_3 \cdot 3H_2O$ were determined as 99.90%. Elemental analyses (C, H and N) were performed on a Vario EL III analyzer. The precision of the elemental analysis is within 5‰. X-ray diffractions were collected with graphite monochromated Mo KR radiation ((λ) 0.71073 Å) on a Bruker CCD diffractometer for $Cr(pyza)_3$ at 298(2) K. TG–DTG–DSC tests were performed on a NETZSCH STA 449 C instrument under a dynamic atmosphere of high

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purity N_2 with a heating rate of 5 °C min^{-1}. UV–visible absorption spectrum was recorded on a Varian Cary 300 spectrometer.

2.2. Preparation

The mixture of Hpyza (3 mmol), $Cr(OH)_3 \cdot 3H_2O$ (1 mmol) and 10 cm^3 ethanol/distilled water (1/1) was boiled and refluxed for 6 h, and the mixed liquid was allowed to evaporate at room temperature for one week. Block-like crystals were filtered and air-dried. Anal. Calc. for the as-prepared crystals: C 42.77%; H 2.15%; O 19.95%; N 22.79%. Found: C 42.75%; H 2.14%; O 19.96%; N 22.80%, which fits with the chemical formula $C_{15}H_9N_6O_6Cr$.

2.3. X-ray crystallography

All diffraction data for the compound were collected on a Bruker Smart-1000 CCD area-detector diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073$) at 293(2) K using the program SMART and processed by SAINT-plus [11]. Absorption corrections were applied by SADABS. The structure was solved by direct methods and refined with full-matrix least-squares technique using SHELXTL. All non-hydrogen atoms were refined anisotropically. All H-atoms were located theoretically and refined. The structural plots were drawn using the SHELXTL and OLEX programs.

2.4. Adiabatic calorimetry

A fully automatic adiabatic calorimeter was used to measure heat capacities over the temperature range $78 \le (T/K) \le 400$. The calorimeter was established in the Thermochemistry Laboratory in the College of Chemistry and Chemical Engineering, Liaocheng University, China. The principle and structure of the adiabatic calorimeter were described in detail elsewhere [12,13]. 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 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 accuracy of the calorimeter, the heat capacities of the reference standard material (α-Al_2O_3) were measured over the temperature range $78 \le (T/K) \le 390$. 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}. Deviations of the experimental results from those of the fitted curve lay within ±0.2%, while the uncertainty was ±0.3%, as compared with the values given by the former National Bureau of Standards [14] 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 [15]. The sample mass used for calorimetric measurements was 2.8742 g, which was equivalent to 0.0068 mol in terms of its molar mass, $M = 421.28$ g mol^{-1}.

2.5. Isoperibol solution–reaction calorimetry

The isoperibol solution–reaction calorimeter consisted 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 were described in detail elsewhere [16].

The thermistor was adopted as the sensor for controlling temperature in the thermostatic bath. But the input signal of the modified high-precision temperature controller (Model: DWT-702, manufactured by Shanghai No. 6 Automated Instrumentation Works), which worked in the PID (proportional–integral–derivative) mode, was not directly from the thermistor sensor, but from the signal of the self-made Wheatstone electric bridge used for temperature controlling. The water was used as the thermostatic media. During whole experiment, the water thermostat was automatically maintained at $T = 298.150 \pm 0.001$ K by regulating an adjustable precision resistor in the Wheatstone bridge. Experiments have demonstrated that the precision of temperature controlling of this kind of system can reach $\pm 1 \times 10^{-3}$ K.

The calorimetric body consisted of the calorimetric chamber, the electric stirrer, the temperature measurement system and the sampling system. The measuring temperature system consisted of a similar Wheatstone electric bridge to that of the controlling temperature system and another thermistor with large negative temperature coefficient of resistance. The thermistor used as thermometer was calibrated on the basis of ITS-90 by the station of Low-temperature Metrology and Measurements, Academia Sinica. A Data Acquisition/Switch Unit (Model: 34970A, Agilent, USA) was used to determine the temperature of the solution in the chamber with an accuracy of 0.1 mK. The unbalanced voltage signal was linear response to the change of temperature over the temperature range from 295 K to 310 K. Measurements [17] indicate that the precision of the temperature measurement system can reach $\pm 1 \times 10^{-4}$ K at least and the time constant of the calorimeter was about 3 s. The system of electric energy calibration consisted of the electric heater and the precision power supply with stepwise constant currents. During each electrical energy calibration, the electrical current through the heater was set at $I = 20.015$ mA, and the resistance of the electrical heater was $R = 1216.9\,\Omega$ at 298.15 K.

The reliability of the calorimeter was verified previously [18] by measuring dissolution enthalpy of KCl (calorimetrically primary standard) in double distilled water at 298.15 K. The mean dissolution enthalpy was 17547 ± 13 J mol^{-1} for KCl, which compared with corresponding published data 17536 ± 3.4 J mol^{-1} [18].

In all dissolution experiments of the samples, 100.00 ml of 0.1 mol dm^{-3} HCl was chosen as the calorimetric solvent.

Finally, UV/vis spectra and the data of the refractive indexes were used to confirm whether initial solution was in the same thermodynamic state as that of the reacted solutions about the two solution systems. These results have indicated that the chemical components and physical–chemistry properties of initial solutions were consistent with those of the reacted solutions.