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Thermochemical study on the Schiff base [H_2salen = *N*,*N*′-bis(salicylidene) ethylendiamine] and its binuclear copper (II) complex

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ABSTRACT

The Schiff-base ligand [H_2salen = *N*,*N*′-bis(salicylidene) ethylendiamine] and the binuclear copper (II) complex [$Cu_2(salen)_2(\mu-O)_2$] were synthesized and the structure of the complex was characterized by X-ray crystallography. Two thermochemical cycles were designed on basis of Hess's law. According to the two cycles, the dissolution enthalpies of relevant substance in the calorimetric solvent of DMF were determined by a solution-reaction isoperibol calorimeter. The measurement experiment was performed at a constant ambient temperature of 298.15 K. After that, the rationality of these two thermochemical cycles was demonstrated by UV spectra and refractive indexes. Base on the measurement results and relevant literature data, the standard molar enthalpies of formation of the Schiff base and the complex were reckoned to be: $\Delta_f H_m^\theta[H_2salen(s),\ 298.15\,K] = -(146.4 \pm 1.9)\,kJ\ mol^{-1}$; $\Delta_f H_m^\theta[Cu_2(salen)_2(\mu-O)_2(s),\ 298.15\,K] = -(171.8 \pm 3.9)\,kJ\ mol^{-1}$.

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1. Introduction

The chemistry of Schiff base and its application have received renewed attention because of their preparative accessibility, diversity and structural variability. Transition–metal complexes coordinated with tetradentate Schiff-base ligands have been studied extensively [1,2]. In particular, salen-type tetradentate ligands (H_2salen = *N*,*N*′-bis(salicylidene)ethylendiamine) have been known since 1933, their complexes became a standard system in coordination chemistry, and their application as inorganic–organic composite materials was investigated [3]. It's also worth mentioning that the copper is one of the essential elements of biological system, which plays an important role in organism. The copper complexes with Schiff base are of considerable interest due to their potential chemical and special biological activities [4–10].

The synthesis of the Schiff base (H_2salen) [H_2salen = *N*, *N*′-bis(salicylidene)ethylendiamine] and the complex [$Cu_2(salen)_2(\mu-O)_2$)] have been reported in published works [3,11–14]. But up to now, their thermodynamic properties has not been in the press. As is known, the thermochemical parameters are an indispensable part of chemical thermodynamics, which closely relates to fundamental academic problems together with application development. In this work, we have planned to prepare the Schiff base (H_2salen) and the complex [$Cu_2(salen)_2(\mu-O)_2$], then further investigated their standard molar enthalpy of formation by the solution-reaction calorimetry, so as to provide some valuable reference data for the further study about the Schiff-base complexes.

2. Experimental

2.1. Materials and physical measurement

All chemicals used herein were analytic grade. Absorption spectra were measured with a Hitachi U-3010 UV/Vis spectrophotometer. FT-IR spectra in KBr (4000–400 cm^{-1}) were recorded at an Avatar 360 spectrometer. Thermochemical analysis was performed using the solution-reaction isoperibol calorimeter (SRC-100, constructed by the thermochemical laboratory of Wuhan University, china). X-ray

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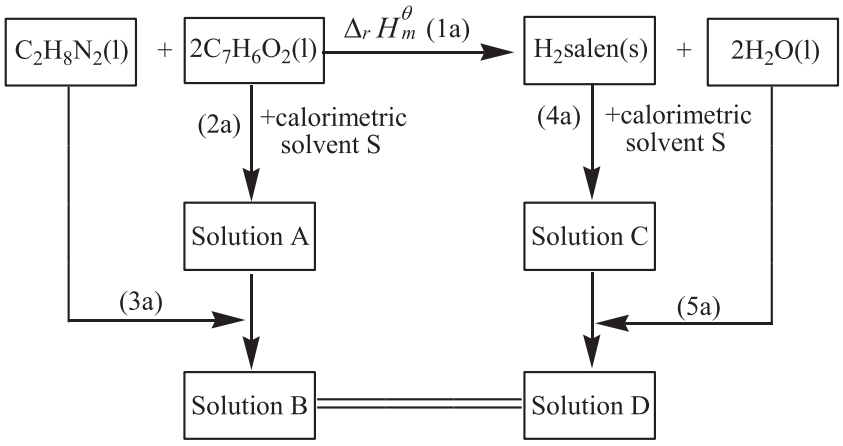

Fig. 1. Thermochemical cycle of reaction (1a).

diffraction measurements were done with a Bruker ApexII Kappa CCD diffractometer using graphite-monochromated Cu-Kα radiation (λ = 0.71073 Å).

2.2. Syntheses of the Schiff -base ligand [13]

The *N*,*N*′-bis(salicylidene)ethylendiamine was prepared by mixing salicylaldehyde and ethylenediamine in ethanol in 2:1 molar ratio, being refluxed for 2 h. The yellow solid formed was filterated after concentration by rotary evaporation to a small volume. The product was purified by recrystallization and dried at 60 °C in a vacuum oven.

2.3. Syntheses of Cu(II) complex [14]

An aqueous solution of NaOH (0.04 g, 1 mmol) was added to the solution of H_2salen (0.1341 g, 0.5 mmol) in 95% ethanol (20 mL). After thirty minutes of stirring, an ethanolic solution of $Cu(CH_3COO)_2{\cdot}H_2O$ (0.0998 g, 0.5 mmol) was slowly added dropwise to the mixed solution at 50 °C for 1 h. The reaction mixture was continuously stirred by a magnetic stirrer for about 2 h. After filtered and recrystalized from ethanol, a green complex was obtained, then dried at 60 °C in vacuo.

2.4. The crystal growth of complex

The prepared complex was dissolved in a mixed solvent of DMF and methanol (V_{DMF}/V_{MeOH} = 5:2) until the solution saturated, followed by filtering through a funnel with cotton (medical grade). One week later, the black-green block crystals were formed in the clear filtrate under the conditions of room temperature. The crystals were characterized by spectroscopic analysis and X-ray crystallographic analysis. The results showed that the formula of complex was $[Cu_2(C_{16}H_{14}O_2N_2)_2]$. On the basis of the formula, purity of the complex was measured by titrate analysis and the result showed its purity was more than 99.0%.

2.5. Solution-reaction isoperibol calorimeter and calibration

The operating principle of solution-reaction isoperibol calorimeter (SRC-100) and its calibration have been described in previous literiature [15]. During the course of this experiment, the system temperature was controlled at 298.15 K by using DWT-702 precise temperature control instrument, the resistance of heater was 1212.3 Ω, and the current was 21.813 mA. The volume of calorimetric solvent in dewar vessel was 100 mL and the dewar vessel was submerged in water thermostat. The precision values of temperature control and temperature measurement were ± 0.001 and ± 0.0001 K, respectively.

This calorimeter is calibrated by measuring the dissolution enthalpies of THAM (NBS 742a, USA) in 0.0001 mol/mL HCl and KCl (calorimetric primary standard) in water at 298.15 K. After five parallel measurements, the average values of dissolution enthalpies for THAM and KCl were $-(29{,}769 \pm 18)$J mol^{-1} and $(17{,}565 \pm 14)$J mol^{-1}, respectively. Comparing with the published data $-(29{,}776 \pm 31.5)$J mol^{-1} for THAM and $(17{,}536 \pm 9)$J mol^{-1} for KCl [15], the eventual error was less than 0.5% and the present calorimeter was very reliable.

2.6. Thermochemical cycle of reaction (1a) and reaction (1b)

The equations of two reactions as follows:

$$2C_7H_6O_2(l) + C_2H_8N_2(l) \rightarrow H_2\text{salen}(s) + 2H_2O(l); \quad (1a)$$

$$2H_2\text{salen}(s) + 2Cu(OAc)_2 \cdot H_2O(s) \rightarrow Cu_2(\text{salen})2(\mu - O)2(s) + 4HOAc(l) + 2H_2O(l) \quad (1b)$$

According to the Hess's law, we have designed the thermochemical cycle for the two reactions (as shown in Figs. 1 and 2). The thermochemical analysis was carried out by an isoperibol calorimeter (SRC-100). After the heat-measurement experiments, we further determined the UV spectra and refractive indexes of solution **B** and **D**. The experimental results indicated that the solution **B** and **D** have same UV spectrum curves (Fig. 3) and equal refractive indexes ($\eta_{25°C}$ = 1.4279). The same case also occurs in solution **2** and **5**, their UV spectrum

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