



The standard molar enthalpy of formation of a new copper(II) Schiff-base complex and its interaction with bovine serum albumin



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ABSTRACT

A new copper(II) Schiff-base complex [Cu(HL)·NO₃·MeOH] was prepared by using equivalent molar of Valen Schiff-base ligand [H₂L=N,N'-ethylene-bis(3-methoxysalicylideneimine)] and Cu(NO₃)₂·3H₂O. The structure of the complex was confirmed by single-crystal X-ray diffraction. Based on an ideal and feasible thermochemical cycle, the standard molar enthalpy of formation of the complex was estimated to be: $\Delta_f H_m^\theta$ [Cu(HL)·NO₃·MeOH(s), 298.15 K] = -(945.40 ± 2.44) kJ mol⁻¹ by an advanced solution-reaction isoperibol calorimeter. In particular, the interaction between the complex and bovine serum albumin (BSA) was investigated using the fluorescence quenching method. Fluorescence quenching data showed that the quenching mechanism of BSA treated by the complex was static quenching, which was highly accord with the non-radioactive energy transfer theory. And some relevant parameters such as binding sites, binding distance and intermolecular forces between the complex and BSA were also obtained by analyzing the fluorescence spectral data.

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1. Introduction

Derived from the condensation reaction of *o*-vanillin and diamines, Valen Schiff-bases and their metal complexes have played an important and popular role in the area of research due to their simple synthesis, versatility, and diverse range of applications such as catalysis, magnetism and pharmacology [1,2]. As typical Salen-like ligands, hexdentate Valen Schiff-bases, which display flexible coordination modes and multiple metal coordination abilities, are usually used as the endogenous bridging units to coordinate with various metal ions such as lanthanide and transition metal ions [3]. Nowadays, the investigations on the medicinal values of Schiff-base complexes have become a new trend, and some Schiff-base complexes have been found to have excellent antibacterial and anti-tumor properties

[4–6]. Researches have shown that some drugs have better effect when they coordinate with some metal ions [7]. Especially, there are a great number of researches on copper(II) complexes with diverse drugs [8–10], which is presumably because of the biological role copper(II) plays and its synergetic activity with drugs [11,12]. Many copper(II) complexes have been confirmed to have a good inhibition effect on several pathogenic fungi and bacteria [13,14].

It is very significant to investigate the synthesis methods, characteristic of molecular structure and various aspects properties of Schiff-base complexes because they may well become one of the most powerful drugs for combating disease of the human body in the future. In this paper, we have prepared a new mononuclear copper(II) Schiff-base complex derived from Valen Schiff-base and Cu(II) salt. And then, its standard molar enthalpy of formation was determined by using a solution-reaction isoperibol calorimeter. Besides, the interaction between the complex and BSA was also investigated by the fluorescence quenching method. These properties of the title complex, we believe, can provide some useful information for further research of Valen Schiff-base complexes, especially in the field of medicine.

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2. Experimental

2.1. Chemicals and instruments

The water used in this work was triply distilled. BSA was purchased from Shanghai Bo'ao Biological Technology Co., Ltd., (Shanghai, China). Other chemicals used in the heat-measurement experiment are listed in Table 1.

The dissolution enthalpies were determined by using a SCR-100 solution-reaction isoperibol calorimeter (constructed by the Thermochemical Laboratory of Wuhan University, China). UV-vis spectra and the fluorescence spectra were obtained on a U-3010 UV-vis spectrophotometer and an F-4600 fluorescence spectrophotometer (Hitachi, Tokyo, Japan), respectively. Refractive indexes were measured by a WAY-IS digital Abbe refractometer (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China). An elemental analyzer (PerkinElmer 2400CHN, USA) was used to measure the C, H, and N contents of the complex. FTIR spectra were recorded with an Avatar360 spectrometer using a KBr pellet in the 400–4000 cm^{-1} range (Nicolet, Madison, USA). X-ray diffraction measurement was carried out on a Bruker SMART CCD diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$).

2.2. Synthesis and single crystal cultivation of the copper(II) Schiff-base complex

The ligand (H_2L) was synthesized by reaction of *o*-vanillin and ethanediamine with a molar ratio of 2:1 in ethanol at room temperature [15]. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.5 mmol, 0.121 g) was added to a methanolic solution (50 mL) of the ligand (0.5 mmol, 0.164 g) at 50 °C. After continuously stirred and refluxed for 2 h, the reaction mixture was filtered, and black-green crystals were formed within few days by slow evaporation of the green filtrate. The crystal structure was characterized by the X-ray diffraction experiment. Elemental analysis for the complex ($\text{C}_{19}\text{H}_{23}\text{CuN}_3\text{O}_8$), Calc. (Found): C 47.06 (47.11), H 4.78 (4.85), N 8.66 (8.63) %.

2.3. Design of thermochemical cycle and selection of calorimetric solvent

Taking Hess's law as the theoretical basis, we designed a thermochemical cycle (as shown in Fig. 1). Obviously, the premise to obtain the precise enthalpy change of Reaction (1) is a highly consistent final state that two sides of the thermochemical cycle must have, in other words, the components of Solution D must be equal to those of Solution G. However, the key issue to reach that state is the selection of calorimetric solvent. An ideal mixed calorimetric solvent S ($V_{\text{DMF}}/V_{\text{HNO}_3} (w_{\text{HNO}_3} : 32.5\%) = 1 : 1$) was prepared through testing for many times, and it can not only

dissolve all of the relevant samples rapidly and completely, but also make two sides of the thermochemical cycle reaching a same final state. The high overlapping UV spectra (Fig. 2) of Solution D' and Solution G', which were obtained by diluting Solution D and Solution G to 25 times with the calorimetric solvent S, and the equal refractive indexes of Solution D and Solution G were the best evidence that they had the same thermodynamic state.

In this way, according to Hess's law, the standard molar enthalpy change of the Reaction (1) can be calculated by means of the dissolution enthalpies of relevant substances in the corresponding calorimetric solvents, which can be determined by using a solution-reaction isoperibol calorimeter. Finally, the standard molar enthalpy of formation of the complex can be obtained by combining the calculated enthalpy change of the Reaction (1) with the literature values of other relevant substances.

2.4. The determination of the dissolution enthalpies

The determination of relevant samples' dissolution enthalpies was conducted by a solution-reaction isoperibol calorimeter (SRC-100). The principle, construction and calibration method of the calorimeter have been elucidated in previous literature [16]. The calibration of the calorimeter was conducted by measuring the dissolution of KCl (calorimetric primary standard, purity greater than 99.99%) in triply distilled water at 298.15 K. The average value of five parallel measurements is $(17,557 \pm 12) \text{ J mol}^{-1}$. Comparing with the published data $(17,536 \pm 9) \text{ J mol}^{-1}$ for KCl [16], the eventual error was less than 0.5% and the present calorimeter was very reliable.

All of the solid samples were dried thoroughly and fully ground. The volume of calorimetric solvent was 100 mL for each time, and the measurement was conducted at 298.15 K. The current of electrical calibration was 21.813 mA and the resistance of the heater was 1212.3 Ω . The sequence of measurements and the corresponding solvents follow the designed thermochemical cycle. All samples were measured for five times and the obtained results were listed in Tables 2 and 3.

2.5. The fluorescence quenching spectra

2.5.1. The preparation of solutions

The preparation of BSA stock solution (5 g L^{-1}): firstly, a precursor solution of NaCl with molar concentration of 0.05 mol L^{-1} was prepared. Then, the appropriate BSA powder was added to the above solution and diluted it to the marked line in a 20 mL volumetric flask. The prepared solution was stored at 1–4 °C in a refrigerator.

The preparation of the complex solution: the complex solution ($100 \text{ mL}, 1 \times 10^{-4} \text{ mol L}^{-1}$) was prepared by dissolving the complex (0.01 mmol) in a DMSO– H_2O mixed solvent ($V_{\text{DMSO}} : V_{\text{H}_2\text{O}} = 1 : 4$).

Table 1
Chemical samples.

Chemical name	Source	Initial mass fraction purity (%)	Purification method	Final mole fraction Purity (%)	Analysis method
The ligand (H_2L)	Self-preparation	–	Recrystallization	99.6	HPLC
The complex [Cu(HL)- $\text{NO}_3 \cdot \text{MeOH}$]	Self-preparation	–	Recrystallization	99.4	Complexometric titration
$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	Sinopharm Chemical Reagent Co., Ltd.	98.5	Recrystallization	99.6	Complexometric titration
HOAc	Sinopharm Chemical Reagent Co., Ltd.	99.7			
MeOH	Sinopharm Chemical Reagent Co., Ltd.	99.8			
NaNO_3	Nanjing Kezheng Chemical Co., Ltd.	99.6			
NaOAc	Nanjing Kezheng Chemical Co., Ltd.	99.5			

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