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Synthesis, spectral characterization and study of thermal behavior kinetics by thermogravimetric analysis of metal complexes derived from salicylaldehyde and alkylamine

Brahim Bouzerafa [b, *], Djouhra Aggoun [a, **], Yasmina Ouennoughi [a], Ali Ourari [a], Ramiro Ruiz-Rosas [c], Emilia Morallon [c], Mohammad S. Mubarak [d]

[a] Laboratoire d'Électrochimie, d'Ingénierie Moléculaire et de Catalyse Redox (LEIMCR), Faculté de Technologie, Université Ferhat ABBAS Sétif-1, 19000, Algeria
[b] Laboratoire de Préparation, Modification et Application des Matériaux Polymériques Multiphasiques (LMPMP), Faculté de Technologie, Université Ferhat ABBAS Sétif-1, 19000, Algeria
[c] Instituto Universitario de Materiales, Universidad de Alicante, Ap. 99, E-03080, Alicante, Spain
[d] Department of Chemistry, the University of Jordan, Amman, 11942, Jordan

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ABSTRACT

Cobalt(III)- and copper(II)-Schiff base complexes have been prepared by reaction of the bidentate Schiff base ligand (HL: 2-(4-methoxyphenyl)-1-iminosalicylidenethane) with cobalt(II) and copper(II) chlorides. Structures of the synthesized complexes have been characterized by various physicochemical techniques, such as IR and UV–Vis spectroscopy, mass spectrometry, thermogravimetric analysis (TG/DTG), and by elemental analysis. Additionally, the redox behavior of the cobalt(III) and copper(II) complexes has been examined by cyclic voltammetry at a glassy carbon electrode in DMF solutions. Thermogravimetric analysis has been employed to evaluate the thermal stability of the prepared complexes $Co^{III}(L)_3 \cdot 1/2H_2O$, $Cu^{II}(L)_2$, in addition to the previously synthesized HL and $Ni^{II}(L)_2$. Furthermore, activation energies of the thermal decomposition were calculated using Kissinger, Ozawa and Coats-Redfern methods. The calculated activation energies were also useful to evaluate kinetic and thermodynamic parameters of the ligand and the corresponding metal complexes including ΔS, ΔH and ΔG. Calculated activation energies follow the order: $E_a(Ni^{II}(L)_2) > E_a(Cu^{II}(L)_2) > E_a(Co^{III}(L)_3 \cdot 1/2H_2O)$.

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1. Introduction

Schiff bases have been extensively used as ligands in the synthesis of metal complexes [1]. In addition, these bases are important in the fields of medicinal and pharmaceutical chemistry [2]. Furthermore, Schiff base metal complexes were found to display interesting bioactivity and play a role as potent drugs in the area of pharmacology [3]. These complexes have been found as potential therapeutic substances [4], anticancer [5], growth-inhibiting agents for a wide range of bacterial strains [6], anti-fungal [7], and antimicrobial [8]. On the other hand, it is generally known that both copper and cobalt are involved in several human metabolisms. In the case of copper, it promotes chemical processes that are combined with other transition metals such as those of Mn(III) and Fe(III) currently involved in catalytic oxidation reactions [9]. In addition, these complexes have been commonly employed as agents for generating active oxygen species for DNA and novel potential DNA targeted as antitumor drugs [10].

The high stability of Schiff base complexes, with metals in different oxidation states, increased their applications in a wide range of fields. They coordinate to metal ions as tetradentate (NNOO), tridentate (NOO), and bidentate (NO) ligands [11–13]. This type of ligands and their metal complexes have been investigated due to their important properties as electrochemical catalysts [14,15]. Some Schiff bases have been employed as excellent homogeneous-and heterogeneous-phase catalysts [3].

In recent years, many areas of chemistry, including the use of spectroscopic techniques for characterization purposes, have significantly advanced. Recently, considerable attention has been

* Corresponding author.
** Corresponding author.
E-mail addresses: bouzer.brah@gmail.com (B. Bouzerafa), aggoun81@yahoo.fr (D. Aggoun).

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paid to the use of thermogravimetric analysis (TG/DTG) as a valuable method to study the thermal stability of new compounds [16–20]. This strategy is often adopted in order to avoid problems, which can arise from increasing the temperature. Accordingly, significant research has been undertaken to understand the thermal characterization of various metal Schiff base complexes and the use of these techniques for identification purposes [21,22]. Additionally, the electrochemical behavior of complexes can provide useful information on catalytic processes because these are accompanied by changes in oxidation state of the metallic center and the structure of the complex [23,24].

We have recently described the synthesis and characterization of a bidentate Schiff base ligand (HL) along with its Ni(II) complex [25]. As a continuation of our work on Schiff base complexes, we describe, herein, the synthesis and characterization of cobalt(III) and copper(II) complexes (Scheme 1). In addition, the present study undertakes the thermal stability of Co(III), Cu(II), and Ni(II) complexes, along with the bidentate ligand HL via thermogravimetric analysis. Furthermore, the various kinetic and thermodynamic parameters of their decomposition steps were also calculated; this will shed some light on the stability of these complexes. Finally, the electrochemical behavior of the cobalt(III) and copper(II) complexes was investigated by cyclic voltammetry.

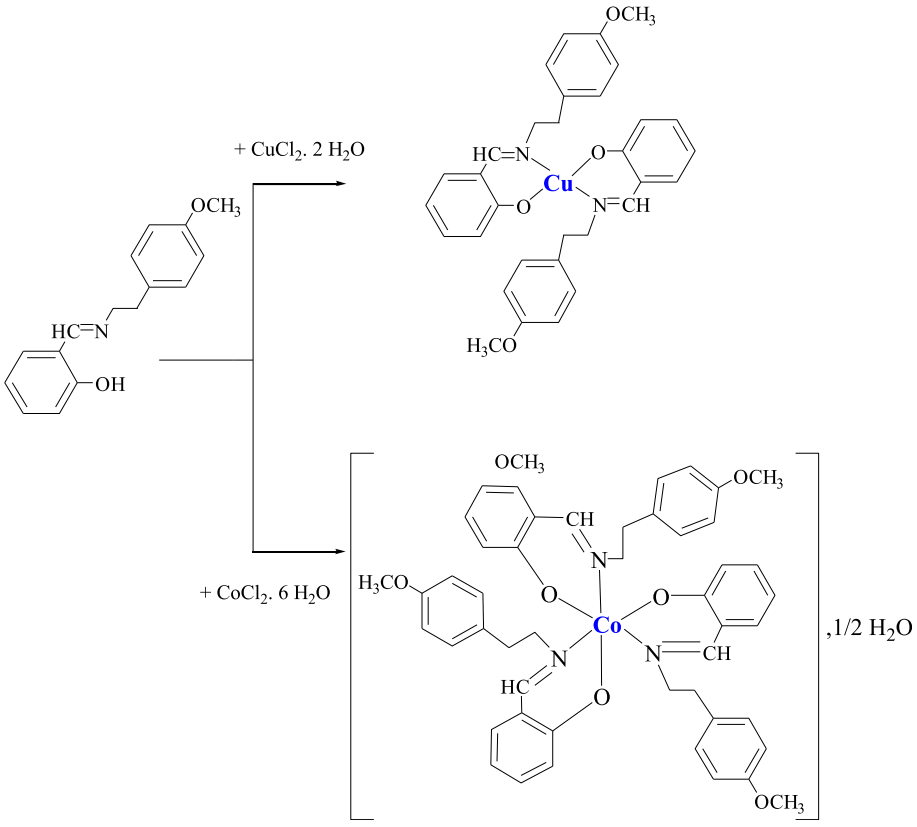
2. Experimental

2.1. Reagents and equipment

Chemicals and reagents used throughout this work were purchased from commercial sources and used as received without further purification. Purity of synthesized compounds was checked with thin layer chromatography (TLC) using glass plates pre-coated with Merck silica gel 60 F254. High resolution mass spectral data (HRMS) were acquired by electrospray ionization technique with the aid of a Bruker APEX-2 instrument. FT-IR spectra of synthesized complexes were recorded, as KBr discs, with a PerkinElmer 1000 FTIR Spectrophotometer in transmittance mode, whereas the UV–visible spectra were obtained using a Unicam UV-300 spectrophotometer. The C, H, and N percentages were determined with a LECO TruSpec Micro CHNS elemental micro-analyzer. We performed cyclic voltammetry experiments in DMF containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$), on a Voltalab 40 Potentiostat-Galvanostat controlled by microcomputer. All measurements were carried out in a 5-cm^3 Metrohm one-compartment cell. The working electrode was a glassy carbon of 3 mm in diameter, whereas a platinum wire served as the counter electrode. Potentials have been quoted with respect to the saturated calomel electrode (SCE). Thermogravimetric analyses (TG and DTG) for the prepared complexes were accomplished using a PerkinElmer TGA 7 analyzer apparatus. Measurements were done at heating rates of 5, 10, 15, and 20 °C min^{-1} under a nitrogen atmosphere over the temperature range of ambient-950 °C.

2.2. Synthesis of the cobalt(III) and copper(II) Schiff base complexes

The Schiff-base ligand, HL, was prepared according to a procedure described in earlier publications [25,26]. Synthesis of the cobalt(III) and copper(II) complexes of the Schiff base ligand was carried out according to the following general procedure: A hot solution of $CoCl_2 \cdot 6H_2O$ or $CuCl_2 \cdot 2H_2O$ (1.0 mmol) in 10 mL of methanol was added to 10 mL methanol solution of the Schiff base ligand (HL, 2 mmol). The mixture was heated, with stirring, at 70 °C for 4 h. The complexes obtained were filtered, washed several times with methanol and then with diethyl ether, and finally dried in a desiccator over anhydrous CaO. Analytical results indicate that the cobalt and copper complexes have (1:3 and 1:2) metal-ligand



Scheme 1. Synthesis protocol of the cobalt(III) and copper(II) complexes.

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