

Spectroscopic investigations of new binuclear transition metal complexes of Schiff bases derived from 4,6-diacetylresorcinol and 3-amino-1-propanol or 1,3-diamino-propane

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Abstract

The bifunctional carbonyl compound; 4,6-diacetylresorcinol (DAR) serves as precursor for the formation of different Schiff base ligands, which are either di- or tetra-basic with two symmetrical sets of either O₂N or N₂O tridentate chelating sites. The condensation of 4,6-diacetylresorcinol with 3-amino-1-propanol (3-AP) or 1,3-diaminopropane (DAP), yields the corresponding hexadentate Schiff base ligands, abbreviated as H₄L_a and H₂L_b, respectively. The structures of these ligands were elucidated by elemental analyses, IR, mass, ¹H NMR and electronic spectra. Reaction of the Schiff base ligands with copper(II), nickel(II), cobalt(II), zinc(II), cadmium(II), iron(III), chromium(III), vanadyl(IV) and uranyl(VI) ions in 1:2 molar ratio afforded the corresponding transition metal complexes. A variety of binuclear complexes for the metal complexes were obtained with the ligands in its di- or tetra-deprotonated forms. The structures of the newly prepared complexes were identified by elemental analyses, infrared, electronic, mass, ¹H NMR and ESR spectra as well as magnetic susceptibility measurements and thermal gravimetric analysis (TGA). The bonding sites are the azomethine and amino nitrogen atoms, and phenolic and alcoholic oxygen atoms. The metal complexes exhibit different geometrical arrangements such as square planar, tetrahedral, square pyramid and octahedral arrangement.
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1. Introduction

A large number of Schiff bases and their metal complexes have been studied because of their interesting and important properties such as their ability to reversibly bind oxygen [1], and their use in catalyses for: oxygenation and oxidation reactions of organic compounds [2], redox systems in biological processes [3], Aldol reactions [4], degradation of dyes through decomposition of hydrogen peroxide and other reagents, in textile industries [5], reduction of thionyl chloride [6] and oxidation of DNA [7]. Also Schiff bases can be used in degradation of organic compounds [8] and in radiopharmaceuticals [9]. For these applications, we are extending this field in synthesis of novel binuclear Schiff base complexes.

The present study, is extension to our work [10,11] where the ligands were prepared by the condensation of

4,6-diacetylresorcinol, as starting material, with 3-amino-1-propanol (3-AP) and 1,3-diaminopropane (DAP) to afford the corresponding Schiff base, H₄L_a and H₂L_b ligands, respectively. The reactions of these ligands with some transition metal ions in molar ratio (1:2, ligand:metal ion) were studied. The newly prepared metal complexes of these ligands were identified by different physicochemical and spectroscopic techniques.

The Schiff base, H₄L_a and H₂L_b ligands were allowed to react with copper(II), nickel(II), cobalt(II), cadmium(II), zinc(II), iron(III), chromium(III), vanadyl(IV) and uranyl(VI) ions. All reactions afforded binuclear complexes except cadmium(II) and zinc(II) for H₄L_a ligand, and zinc(II) and iron(III) for H₂L_b ligand, which gave oily products which were difficult to isolate. For the former ligand, the copper(II) complex exhibits a square planar geometry, while nickel(II), cobalt(II) and iron(III) complexes exhibit an octahedral geometry which contain nitrate ions acting as unidentate ligands, also, the chromium(III) complex showed an octahedral geometry but the nitrate ions acting as bidentate ligand. The vanadyl(IV) complex showed a square pyramidal geometry and the uranyl(VI) complex has a coordination number = 8. The bonding sites are the azomethine nitrogen atoms and

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the phenolic and alcoholic oxygen atoms. For the H_2L_b ligand, all complexes having octahedral environment around Cu(II), Ni(II), Co(II), Fe(III) Cr(III), VO(IV) and UO₂(VI) ions. The bonding sites are the azomethine and amino nitrogen atoms and the phenolic oxygen atoms, except uranyl(VI) complex, where the amino nitrogen atoms are not involved in the coordination. Most of the complexes of the H_2L_b ligand contain nitrate ions which acting as unidentate ligands, also, in case of vanadyl(IV) complex, the SO_4^{2-} ions is involved in the coordination and acts as a bridged ligand.

2. Experimental

2.1. Materials

Resorcinol, acetic anhydride, zinc chloride, 3-amino-1-propanol and 1,3-diaminopropane were either Analar or Merck. Copper(II), nickel(II), cobalt(II), cadmium(II), zinc(II), iron(III) and chromium(III) were used as nitrate salts and were Merck or BDH. Uranyl(VI) acetate dihydrate and vanadyl(IV) sulphate monohydrate were Merck or BDH. Organic solvents (ethanol, absolute ethanol, methanol, diethylether, acetone, dimethylformamide (DMF) and dimethylsulfoxide (DMSO)) were reagent grade.

2.2. Synthesis of the Schiff base ligands

Schiff base ligands were prepared in two steps. The first step was the formation of 4,6-diacetylresorcinol (DAR) by acetylation of resorcinol. The second step was the condensation of 4,6-diacetylresorcinol (DAR) stoichiometrically in a molar ratio 1:2 with 3-amino-1-propanol or 1,3-diaminopropane in absolute ethanol. The Schiff base ligands were formed by stirring the reaction for 1 h at room temperature. If the ligand did not precipitate, the reaction was heated to reflux for 1–3 h, where the solid was formed.

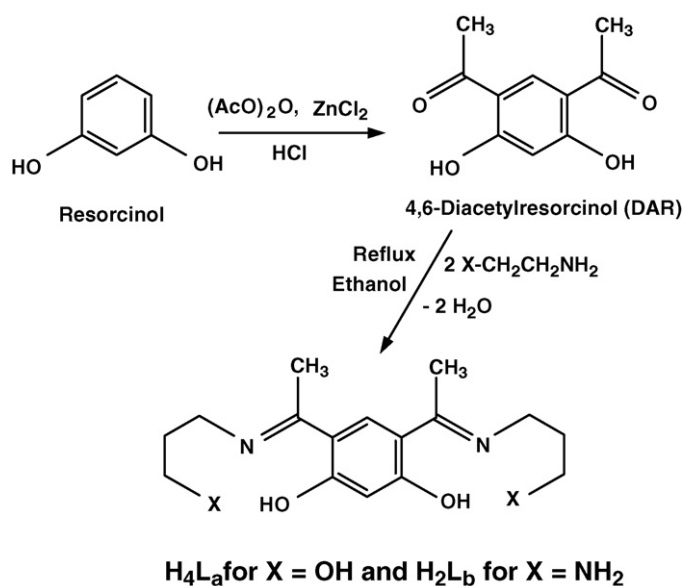
The Schiff base, H_4L_a and H_2L_b ligands were characterized by elemental analysis, ¹H NMR spectroscopy and UV–vis spectrophotometer in DMF or DMSO and in the solid state by FT-IR and mass spectroscopy. The synthetic steps are given in details as follows.

2.2.1. Synthesis of 4,6-diacetylresorcinol

The method of preparation was the same as mentioned in Ref. [10]. The yield was 10.0 g (28.4%), mp 178–180 °C. 4,6-Diacetylresorcinol was characterized by elemental analysis and infrared spectrum.

2.2.2. Synthesis of the Schiff base, H_4L_a and H_2L_b ligands

The H_4L_a and H_2L_b ligands were synthesized by adding 4,6-diacetylresorcinol, DAR (3.88 g, 20.0 mmol) dissolved in hot absolute ethanol (30 mL) to 3-amino-1-propanol (3.00 g, 40.0 mmol) or 1,3-diaminopropane (2.96 g, 40.0 mmol) in absolute ethanol (30 mL). The reaction mixtures were heated to reflux for 1–3 h. The yellow products obtained were filtered off and washed with few amounts of ethanol then diethylether and air dried. Fine crystals were obtained by recrystallization



Scheme 1. Schematic representation for the formation of the Schiff base, H_4L_a and H_2L_b ligands. Structure 1. Representative structures of the Schiff base, H_4L_a and H_2L_b ligands.

from ethanol. The ligands were kept in a desiccator until used. The yield was 5.00 g (81.0%), and 4.80 g (78.1%), for H_4L_a and H_2L_b , respectively. The melting point (mp) for both ligands were >280 °C.

The reaction for the formation of 4,6-diacetylresorcinol and their corresponding H_4L_a and H_2L_b ligands are illustrated in Scheme 1.

2.3. Synthesis of the Schiff base metal complexes

Methanolic solutions of the metal salts (30 mL) were added gradually to methanolic solutions of the deprotonated ligand (60 mL) in the molar ratio 2:1. Triethylamine, Et₃N, was used to affect the deprotonation of the ligands. The reaction mixture of the deprotonated H_4L_a ligand with metal salts was stirred on cold for 1–3 h, while the reaction mixture of the other ligand, H_2L_b , was heated to reflux for 2–3 h. The time of reflux depends on the formation of the solid products on either hot or cold. The resulting precipitates were filtered off, washed with methanol then ether. Most of the complexes are insoluble in most common organic solvents, but some of them are partially soluble in DMF and/or DMSO.

In each case, the ligand is deprotonated using Et₃N. In the case of H_4L_a ligand, Et₃N (1.212 g, 12 mmol) dissolved in methanol (20 mL) was added to 3 mmol of the ligand in 30 mL methanol, i.e., in the molar ratio 4:1 (Et₃N:ligand) and heated to reflux for 30 min. The appropriate weight (6 mmol) of the metal salts was added to the ionic deprotonated ligand to form the metal complexes. In the case of H_2L_b , the same procedure was used, however, the molar ratio was 2:1 (Et₃N:ligand).

The following detailed preparations are given as examples and the other complexes were obtained similarly.

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