Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 122 (2014) 676–681

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis, characterization, and thermodynamics of some new unsymmetrical Schiff bases of salicylaldehyde with 3,4-diaminopyridine and their cobalt(III) complexes

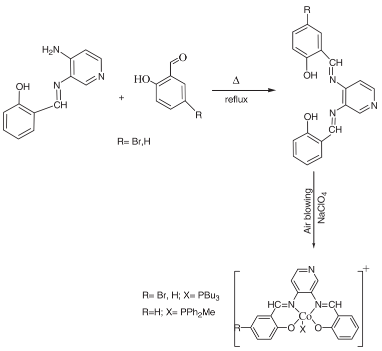
Mozaffar Asadi [a,*], Susan Torabi [a,b], Khosro Mohammadi [c]

[a] Chemistry Department, College of Sciences, Shiraz University, Shiraz 71454, Islamic Republic of Iran
[b] International Branch, Shiraz University of Medical Sciences, Shiraz, Islamic Republic of Iran
[c] Chemistry Department, Faculty of Sciences, Persian Gulf University, Bushehr 75169, Islamic Republic of Iran

HIGHLIGHTS

- Synthesis and characterization of unsymmetrical cobalt(III) Schiff base complexes.
- Thermodynamic studies of their interactions with various donors.
- Investigation the effects of different electronic and steric characters of the ligand's substituent.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 July 2013
Received in revised form 8 September 2013
Accepted 26 September 2013
Available online 9 October 2013

Keywords:
Cobalt(III)
Unsymmetrical Schiff base
Thermodynamic free energy change
Formation constants

ABSTRACT

Some new Schiff bases derived from 3,4-diaminopyridine (3,4-DAP) and their new unsymmetrical Co(III) five coordinate complexes described as $[Co(Chel)(L)]ClO_4{\cdot}H_2O$ where (Chel) is the deprotonated form of a series of unsymmetric ligands containing 3,4-diaminopyridine (3,4-DAP) and substituted salicylaldehyde moieties and a new Co(III) six coordinate Co(III) complex, were synthesized and characterized by ^{1}H NMR, IR, UV–Vis, and elemental analysis. For the new synthesized five coordinate complexes, the formation constants of the interaction of the Co(III) Schiff bases with various donors were measured spectrophotometrically. The trend of the formation constants of the five coordinate Co(III) Schiff base complexes toward a given phosphine is as follow: 5-H > 5-Br and the formation constants trend of these donors are as follow: $PBu_3 > PPh_2Me$. Furthermore the adduct formation of the five coordinate $[Co(3,4\text{-Sal-pyr})(PBu_3)]\ ClO_4{\cdot}H_2O$, with aromatic amines shows the following binding trend: Im > 2-MeIm > 2-EtIm > BzIm. The trend of the formation constants of Co(III) Schiff base complexes toward a given donor according to the phosphine axial ligand is as follow: $PBu_3 > PPh_2Me$.

Introduction

Metal Schiff base complexes have contributed widely to the inorganic chemistry of chelate systems. Metal complexes of these organic ligands have been studied for a long time. The Schiff bases involving a pyridine ring have received considerable attention in literature [1,2]. The anti-inflammatory activity of 2-salicylideneaminopyridine and the corresponding complex with Co(II) has been reported [3].

Schiff bases derived from 3,4-diaminopyridine (3,4-DAP) have received much less attention [4,5], although many clinical studies

---

* Corresponding author. Tel.: +98 2284822; fax: +98 (711)2286008.
E-mail addresses: mozaffarasadi@yahoo.com, asadi@susc.ac.ir (M. Asadi).

1386-1425/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2013.09.098

of DAP suggest that this amine, known as a K^+ channel blocker [6–8], effectively relieves the symptoms of various neurological disorders such as the Lambert–Eaton myasthenia syndrome (LEMS) [9–11]. In order to better understand the properties of isomers of diaminopyridines, we studied the thermodynamics property of their cobalt(III) complexes. In particular, we are interested in comparing some thermodynamic features of new synthesized Schiff bases derived from 3,4-DAP with our previously investigated Schiff bases obtained from 2,3-DAP [12].

Recently we reported the thermodynamic properties of cobalt Schiff base complexes with (N,N′-bis(Salicyliden)-2,3-diaminopyridine) as ligand [12]. Sustained interest in the characteristics of the Schiff bases derived from diaminopyridines has promoted us to prepare condensation products of 3,4-DAP and various salicylaldehyde (1, 2, Fig. 1S). This report deals with their detailed characteristic, including characterization and thermodynamic properties of some new unsymmetrical cobalt(III) complexes derived from 3,4-DAP. Comparison of their properties, spectrally, and thermodynamically aimed to investigate the effects of different electronic and steric situations.

Experimental

Materials

All chemicals were used as obtained from Merck, Fluka or Aldrich. Anal. Grade solvent from Merck was used without further purification. The diamine and salicylaldehyde were distilled before use.

Apparatus and techniques

The infrared spectra of all ligands and their complexes were recorded in the range 4000–400 cm^{-1} using a Shimadzu FTIR-8300 spectrophotometer applying the KBr disc technique. The UV–Vis absorption spectra were recorded using Perkin–Elmer Lambda 2 spectrophotometer at room temperature. The Elemental analysis was carried out by Thermo Finnigan-Flash-1200. The ^1H NMR spectra were recorded by a Bruker Avance DPX 250 MHz spectrometer.

Preparation of the Schiff bases

A mono Schiff base **(1)** was prepared by mixing stoichiometric amounts of analytically pure salicylaldehyde with 3,4-diaminopyridine dissolved in ethanol and refluxing for three hours on a water bath. The separated brownish yellow crystals were recrystallized from hot ethanol [13]. Such compound as **(1)**, commonly referred to as half-unit, is a potential precursor for the synthesis of non-symmetrical Schiff bases comprising 3,4-DAP moieties. By mixing the half unit with appropriate aldehyde in the 1:1 ratio, using the same condensation procedure the bis-Schiff bases **(2)**, **(3)** were obtained. After evaporation of the resulting solution to the half volume the separated crystals were filtered off and recrystallized from ethanol.

Synthesis of cobalt complexes

Synthesis of the five coordinate Co(III) complexes

The cobalt(III) Schiff base complexes were prepared by the methods described in the literature [14], to a refluxing solution of tetradentate ligands (1 mmol), in methanol (10 cm^3) were added $Co(OAc)_2{\cdot}4H_2O$ (0.25 g, 1 mmol). After 15 min, tri-n-butylphosphine (0.2 cm^3, 0.8 mmol) was added to the solution. The reaction mixture was refluxed for an hour. The Co(II) formed complex was oxidized by blowing air into the solution for 2 h, and the solution was filtered. An appropriate amount of sodium perchlorate was added to the filtrate. The resulting brown crystals were formed after 48 h. The crystals were washed with some methanol and were purified by re-crystallization in dichloromethane/ethanol. The complex was dried in vacuum at $T = 323$ K for 48 h (Fig. 2S).

Synthesis of the six coordinate Co(III) complex, $[Co(3,4\text{-}Salpyr)(PBu_3)_2]ClO_4{\cdot}H_2O$ (7)

To a methanolic solution (6 ml) of the ligand 3,4-Salpyr (0.16 g, 0.5 mmol) and tributylphosphine (0.4 ml, 1.6 mmol) was added a methanolic solution (1.5 ml) of $Co(OAc)_2{\cdot}4H_2O$ (0.136 g, 0.6 mmol). The reaction mixture was refluxed for 2 h to give a brownish red solution. A methanolic solution (7 ml) of $NaClO_4{\cdot}H_2O$ (0.42 g, 3 mmol) was then added and the mixture was stirred for 2 h. The resulting brown precipitate was collected by filtration and recrystallized by dichloromethane/methanol. The product **(7)** was dried under vacuum.

Thermodynamic studies

The formation constants have been determined by UV–Vis absorption spectroscopy from the reaction of the acceptors with the donors in 96% methanol solvent, according to the following equations:

$$[Co(3,4\text{-}Salpyr)(L)]^+ + Y \rightleftarrows [Co(3,4\text{-}Salpyr)(L)Y]^+ \quad (1)$$

where L = PBu_3, PPh_2Me and Y = n-butylamine, PPh_2Me and PBu_3

$$[Co(5\text{-}Br\text{-}3,4\text{-}Salpyr)(PBu_3)]^+ + Y \rightleftarrows [Co(5\text{-}Br\text{-}3,4\text{-}Salpyr)(PBu_3Y)]^+ \quad (2)$$

where Y = PPh_2Me and PBu_3

$$[Co(3,4\text{-}Salpyr)(PBu_3)]^+ + Y \rightleftarrows [Co(3,4\text{-}Salpyr)(L)Y]^+ \quad (3)$$

where Y = Im, 2-MeIm, 2-EtIm and BzIm.

A solution from each complex with concentration at about 3×10^{-5} M and constant ionic strength ($I = 0.1$ M) by sodium perchlorate was prepared. In a typical titration 2.5 ml of this solution was transferred into the thermostated cell compartment of the UV–Vis instrument, which was kept at constant temperature (±0.1 K) by circulating water and was titrated by the given donor. The titration was done by adding aliquots of the donor with a Hamilton microlitre syringe. The donor's concentration was varied in 1–3 folds in excess.

The absorption measurements were carried out at various wavelengths where the difference in absorption was the maximum

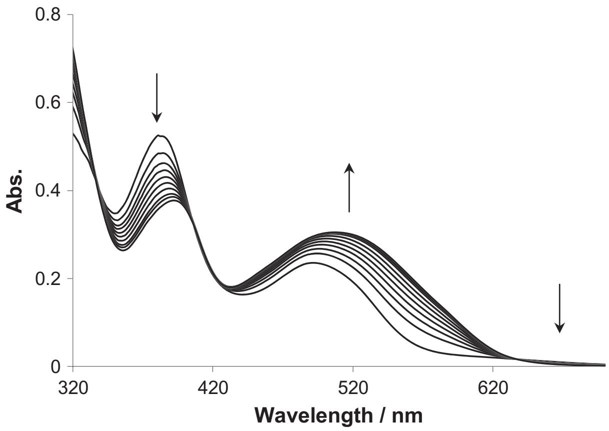


Fig. 1. The variation of the electronic spectra of $[Co(3,4\text{-}Salpyr)(PBu_3)]ClO_4{\cdot}H_2O$ titrated by PBu_3 at $T = 293$ K in 96% methanol.