Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 122 (2014) 179–185

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

New 3,4-diaminobenzoic acid Schiff base compounds and their complexes: Synthesis, characterization and thermodynamics

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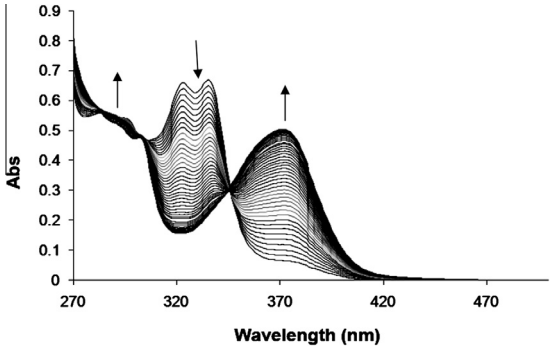
HIGHLIGHTS

- Schiff base ligands of 3,4-diaminobenzoic acid derivaties (L) have been synthesized and characterized.
- The their metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) were prepared.
- The formation constants are increased according to the sequence: $Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$.

GRAPHICAL ABSTRACT

Some new tetradentate Schiff base ligands (L) and their metal complexes were prepared via condensation of 3,4-diaminobenzoic acid with 2-hydroxybenzaldehyde derivatives, Khosro Mohammadi, Mahmood Niad and Tahereh Jahfari



ARTICLE INFO

Article history:
Received 18 July 2013
Received in revised form 27 October 2013
Accepted 31 October 2013
Available online 14 November 2013

Keywords:
3,4-Diaminobenzoic acid
Salicylaldehyde derivatives
Tetradentate Schiff base
Complexation
Formation constant

ABSTRACT

Some new tetradentate Schiff base ligands (H_3L) were prepared via condensation of 3,4-diaminobenzoic acid with 2-hydroxybenzaldehyde derivatives, such as 3,4-bis((E)-2,4-dihydroxybenzylideneamino)benzoic acid (H_3L^1), 3,4-bis((E)-2-hydroxy-3-methoxybenzylideneamino)benzoic acid (H_3L^2) and 3,4-bis((E)-5-bromo-2-hydroxybenzylideneamino)benzoic acid (H_3L^4). Additionally, a tetradentate Schiff base ligand 3,4-bis((E)-2-hydroxybenzylideneamino)benzoic acid (H_3L^3) and its complexes were synthesized. Their metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) were prepared in good yields from the reaction of the ligands with the corresponding metal acetate. They were characterized based on IR, ^{1}H NMR, Mass spectroscopy and UV–Vis spectroscopy. Also, the formation constants of the complexes were measured by UV–Vis spectroscopic titration at constant ionic strength 0.1 M ($NaClO_4$), at 25 °C in dimethylformamide (DMF) as a solvent.

Introduction

Schiff bases have been used extensively as ligands in the field of coordination chemistry. Some of the reasons are that the intramolecular hydrogen bonds between the (O) and the (N) atoms, which play an important role in the formation of metal complexes, and that Schiff base compounds show photochromism and thermochromism in the solid state by proton transfer from the hydroxyl (O) to the imine (N) atoms [1]. Schiff bases derived from aromatic amines and aromatic aldehydes and their metal complexes are widely applicable in inorganic, biological and analytical chemistry. Schiff bases have improved conservative reactions such as allylic alkylation, the hydrosilation of acetophenones, the decomposition of hydrogen peroxide, Michael addition, annulations,

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1386-1425/$ - see front matter
http://dx.doi.org/10.1016/j.saa.2013.10.103

carbonylation, Heck reaction, benzylation of alanine, amidation and the aziridination of hydrocarbons, the isomerization of norbornadiene to quadricyclane, the addition of cyanides to imine, cyclopropanation, the silylcyanation of aldehydes, the desymmetrization of *meso* compounds, Diels–Alder reaction, and aldol condensation reaction[2–5].

Schiff bases are an important class of compounds in medicinal and pharmaceutical field. They show biological applications including antibacterial [6,7], antifungal [8] and antitumor activity [9].

The main purpose of the present article is to study the structural characterization of Schiff base ligands and their metal complexes and the behavior of Schiff bases towards Co(II), Ni(II), Cu(II) and Zn(II) ions.

Experimental

Materials and reagents

All the chemicals used were of the analytical reagent grade (AR), and of highest purity available. They included 3,4-diaminobenzoic acid, 2-hydroxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde, 2-hydroxy-3-methoxybenzaldehyde, 2,4-dihydroxybenzaldehyde, nickel (II) acetate tetrahydrate, cobalt (II) acetate tetrahydrate, copper (II) acetate monohydrate and zinc (II) acetate dihydrate. All the materials and organic solvents including absolute methanol, ethyl acetate, n-hexane, chloroform and dimethylformamide were commercially obtained from Merck, Aldrich or Fluka.

Physical measurements

Purity of the products was checked by TLC in a mixture of ethyl acetate and n-hexane solvent system. Infrared spectra were measured from 4000 to 400 cm^{-1} as KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. The NMR spectra were scanned on a Bruker Avance DPX-400 spectrometer by using DMSO-d_6 as a solvent and TMS as an internal standard at 400 MHz. Mass spectra of the compounds were scanned on a Shimadzu LCMS-2010EV instrument. UV–Vis measurements were carried out in Perkin–Elmer Lambda 25 UV–Vis spectrophotometer. Melting points were measured in capillary tubes using a Buchi 535 melting point apparatus.

Synthesis of Schiff bases (H_3L)

All the new tetradentate Schiff base ligands (H_3L^1, H_3L^2 and H_3L^4) were synthesized by condensing 1 mmol of 3,4-diaminobenzoic acid and 2 mmol of substituted aldehyde [(2,4-dihydroxybenzaldehyde, 2-hydroxy-3-methoxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde] in methanol (30 mL) at reflux temperature for 2–3 h (See Scheme 1). The products were then poured by wash well water and chloroform and filtered. The purity was checked by TLC in a mixture of n-hexane and ethyl acetate solvent system and finally dried at 70 °C in an oven. The H_3L^3 Schiff base ligand and its complexes were prepared according to a previously published method [10] (See Scheme 1). The details for the synthesis of the new Schiff base ligands (H_3L^1, H_3L^2 and H_3L^4) are presented in Table 1.

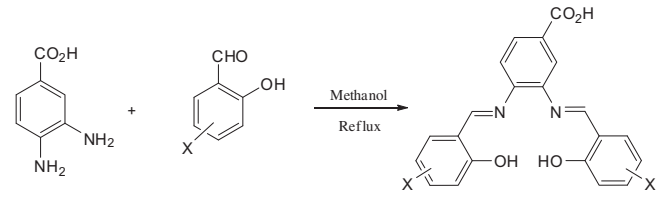
Synthesis of the metal complexes

The synthesis methods of the new metal complexes are as follow: Metal (II) acetate (1 mmol) dissolved in methanol (20 ml) was reacted with a methanol solution (20 ml) of Schiff base ligands (H_3L^1 and H_3L^2) (1 mmol) and Metal (II) acetate (1 mmol) dissolved in DMSO (20 ml) was reacted with a DMSO solution (20 ml) of Schiff base ligand (H_3L^4) (1 mmol) by refluxing for 1 h. The solid products were formed. Analytically pure products can be obtained by being washed well with methanol (to remove metal), filtered and dried in vacuum. The details for synthesis of the new metal complexes are presented in Table 1.

Results and discussion

^{1}H NMR spectra

The chemical shifts of the different types of protons in the ^{1}H NMR spectra of the H_3L ligands and the metal complexes of [M(HL)] were reported in Table 2. For all the complexes, the coordination of the phenolic oxygens to metal was confirmed by



Abbreviation	Name
H_3L^1 (X=4-OH)	3,4-bis ((E)-2,4-dihydroxybenzylideneamino)benzoic acid
H_3L^2 (X=3-OMe)	3,4-bis ((E)-2-hydroxy-3-methoxybenzylideneamino)benzoic acid
H_3L^3 (X=H)	3,4-bis ((E)-2-hydroxybenzylideneamino)benzoic acid
H_3L^4 (X=5-Br)	3,4-bis ((E)-5-bromo-2-hydroxybenzylideneamino)benzoic acid
[Co(HL^1)] (1)	(3,4-bis ((E)-2,4-dihydroxybenzylideneamino)benzoic acid)cobalt (II)
[Ni(HL^1)] (2):	(3,4-bis ((E)-2,4-dihydroxybenzylideneamino)benzoic acid)nickel (II)
[Cu(HL^1)] (3)	(3,4-bis ((E)-2,4-dihydroxybenzylideneamino)benzoic acid)copper (II)
[Zn(HL^1)] (4)	(3,4-bis ((E)-2,4-dihydroxybenzylideneamino)benzoic acid)zinc (II)
[Co(HL^2)] (5)	(3,4-bis ((E)-2-hydroxy-3-methoxybenzylideneamino)benzoic acid)cobalt (II)
[Ni(HL^2)] (6)	(3,4-bis ((E)-2-hydroxy-3-methoxybenzylideneamino)benzoic acid)nickel (II)
[Cu(HL^2)] (7)	(3,4-bis ((E)-2-hydroxy-3-methoxybenzylideneamino)benzoic acid)copper (II)
[Zn(HL^2)] (8)	(3,4-bis ((E)-2-hydroxy-3-methoxybenzylideneamino)benzoic acid)zinc (II)
[Co(HL^3)] (9)	(3,4-bis ((E)-2-hydroxybenzylideneamino)benzoic acid)cobalt (II)
[Cu(HL^3)] (10)	(3,4-bis ((E)-2-hydroxybenzylideneamino)benzoic acid)copper (II)
[Zn(HL^3)] (11)	(3,4-bis ((E)-2-hydroxybenzylideneamino)benzoic acid)zinc (II)
[Co(HL^4)] (12)	(3,4-bis ((E)-5-bromo-2-hydroxybenzylideneamino)benzoic acid)cobalt (II)
[Ni(HL^4)] (13)	(3,4-bis ((E)-5-bromo-2-hydroxybenzylideneamino)benzoic acid)nickel (II)
[Cu(HL^4)] (14)	3, 4-bis ((E)-5-bromo-2-hydroxybenzylideneamino)benzoic acid)copper (II)
[Zn(HL^4)] (15)	(3,4-bis ((E)-5-bromo-2-hydroxybenzylideneamino)benzoic acid)zinc (II)

Scheme 1.