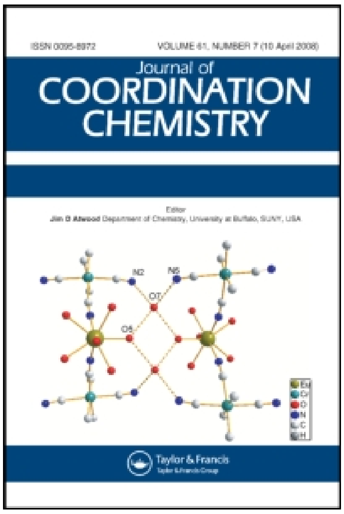

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Studies on the complexing behavior of a potentially tetradentate Schiff-base ligand with some transition metal ions

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To cite this Article Nair, M. Sivasankaran and Raj, C. Ravi Samuel(2009) 'Studies on the complexing behavior of a potentially tetradentate Schiff-base ligand with some transition metal ions', Journal of Coordination Chemistry, 62: 17, 2903 — 2908

To link to this Article: DOI: 10.1080/00958970902946694

URL: http://dx.doi.org/10.1080/00958970902946694

Journal of Coordination Chemistry
Vol. 62, No. 17, 10 September 2009, 2903–2908

Studies on the complexing behavior of a potentially tetradentate Schiff-base ligand with some transition metal ions

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(*Received 9 October 2008; in final form 6 February 2009*)

The Schiff base furfural-histidine with Co(II), Ni(II), Cu(II), and Zn(II) in solution gives M(AB), M(AB)B, or $M(AB)_2$. The Schiff base is tetradentate in $M(AB)_2$ and M(AB)B and tridentate in $M(AB)_2$; $[M(AB)_2]\cdot 2H_2O$ ($M = Co, Ni$ and Zn) and $[Cu(AB)]NO_3$ were synthesized and characterized by elemental analysis, molecular weight determination, conductance, IR, UV–Vis, and CV. The electronic spectral measurements indicate that $M(AB)_2$ ($M = Co(II)$ and Ni(II)) are octahedral and Cu(AB) is square planar geometry. The donor groups in the complexes have been identified by IR. The complexes undergo irreversible one step, two-electron reduction. Antibacterial activity of the complexes was screened for *Escherichia coli* and *Staphylococcus aureus*. Cu(II) complex was found to be more active than the Co(II), Ni(II), and Zn(II) complexes.

Keywords: Computation; *Ab initio*; Potentiometry; Schiff base; Furfural; Histidine; IR; UV–Vis; CV; Antibacterial

1. Introduction

Schiff bases are of interest due to applications in analytical chemistry, medicine, industry, photonics, and catalysis [1, 2]. Heterocyclic compounds are used as pharmaceuticals, pesticides, herbicides, dyes, and plastics [3]. Oxy-heterocyclic compounds are found in many plants and animals. Furfural is a well-known oxy-heterocyclic natural compound used in vegetable oil, petroleum, plastic, rubber, and cosmetic industries [4]. Schiff-base complexes of furfural have antibacterial, antifungal, and antitumor activities [5, 6]. The present article reports the complexing behavior of furfuralhistidinate (furfural-his) derived from furfural and histidine(his) with Co(II), Ni(II), Cu(II), and Zn(II) and their antibacterial activity towards *Escherichia coli* and *Staphylococcus aureus*.

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970902946694

2. Experimental

All chemicals were of AnalaR grade. Solution studies were carried out by batch-wise pH titration as described earlier [7]. The stability constants for the various Schiff-base complexes were evaluated using the computer program SCHIFF [8]. The complexes were synthesized by metal template method [9]. Attempts to crystallize the complexes for X-ray single crystal analysis were not successful. Molar conductance of the complexes in DMSO was measured at $27 \pm 0.1^{\circ}C$ with a digital conductivity bridge (M/s. M.S. Electronics, model 601E). Electronic spectral measurements were made using a Perkin–Elmer UV–Visible model Lambda 3B spectrophotometer. Infrared spectra were recorded on a JASCO FT-IR-410 spectrophotometer (4000–400 cm^{-1}). Cyclic voltammetric measurements were carried out on a Bio-Analytical System model CV-50 W with a three electrode cell comprising a reference Ag/AgCl, auxiliary platinum, and working glassy carbon electrodes. Antimicrobial activity of the complexes was tested for growth inhibition against *E. coli* and *S. aureus* using paper disc technique [10].

3. Results and discussion

3.1. *Solution state studies*

Stability constant studies were carried out in the pH range of 6.0 to 9.0. Three types of ternary species, MAB, MAB_2, and MA_2B_2, were detected in the Co(II), Ni(II), and Zn(II)-furfural-his systems, while only MAB was present in the Cu(II) system. The stability constant values are given in table 1.

MAB can be either mixed ligand or Schiff-base complexes. The calculated overall formation constants of the mixed ligand complexes, MAB, are 8.70, 9.44, 10.47, and 7.61 log units, respectively, for $M = Co(II)$, Ni(II), Cu(II), and Zn(II) (experimental values 13.16, 15.33, 19.92, and 13.24 log units). This large increase in stability shows that MAB is a Schiff-base complex, M(AB), and not a mixed ligand complex, MAB. The experimental stability constant values are in the range expected for tetradentate binding of furfural-his through imino and imidazole nitrogens and carboxylato and furan oxygens. The M(AB) species can be stable with two five- and one six-membered chelate rings. The calculated values of the stabilization constant, $\Delta \log K_{MAB}$ [9] for Co(II), Ni(II), Cu(II), and Zn(II) systems are, respectively, 4.43, 4.74, 7.25, and 4.94, following the Irving–Williams order of stability [11].

The ternary species MAB_2 in the Co(II), Ni(II), and Zn(II) systems can be represented as M(AB)B [12], where the Schiff-base ligand (AB) is tetradentate.

Table 1. Stability constants for the M(furfural-his)(AB) Schiff-base complex systems.

Parameter	Co(II)	Ni(II)	Cu(II)	Zn(II)
$\log \beta_{M(AB)}$	14.28	15.33	19.92	13.24
$\log \beta_{M(AB)B}$	18.47	22.13	–	18.31
$\log \beta_{M(AB)_2}$	20.38	24.36	–	20.45
$\Delta \log K_{M(AB)}$	5.55	6.03	7.25	4.94

The MA_2B_2 species can be represented as $M(AB)_2$, where both the Schiff base-ligands (AB) are tridentate.

Electronic spectra for Co(AB) and $Co(AB)_2$ were recorded, respectively, at pH 7.0 and 7.5 in aqueous solution. For CoAB, the absorption maximum occurs at 638 nm, attributed to $^4A_2(F) \rightarrow {}^4T_1(P)$ for tetrahedral Co(II) [13]. The $Co(AB)_2$ has two bands, one at 467 nm and the other at 759 nm showing octahedral transitions $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ [13].

The spectra of Ni(AB) and $Ni(AB)_2$ were recorded at pH 7.2 and 7.8, respectively, in aqueous solution. The Ni(AB) species has absorption at 647 nm for $^3T_1(F) \rightarrow {}^3T_1(P)$ of tetrahedral geometry. The 1 : 2 complex has three absorptions at 323, 604, and 878 nm, respectively, for $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, indicating octahedral geometry [13]. Cu(AB) shows a broad band at 641 nm corresponding to merged transitions of $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{z^2}$ indicating square-planar geometry [13].

3.2. *Solid state studies*

The complexes are well-defined solids with high decomposition temperatures, air and moisture stable. The colors of the complexes and analytical data are given in table 2. The experimental molecular weights are comparable with theoretical values. The low molar conductance for Co(II), Ni(II), and Zn(II) complexes indicate non-electrolytes while conductance of 48.6 $Ohm^{-1}\,cm^{-2}\,mol^{-1}$ for the Cu(II) complex shows 1 : 1 electrolytic nature [14]. Based on elemental analysis and molar conductance data Co(II), Ni(II), and Zn(II) complexes can be represented as $[M(furfural\text{-}his)_2] \cdot 2H_2O$. The Cu(II) complex is $[Cu(furfural\text{-}his)] \cdot NO_3$.

3.2.1. IR spectral studies. IR spectral data are given in table 3. Strong bands in the 3400–3100 cm^{-1} region are assigned to $\nu_{O–H}$ and/or $\nu_{N–H}$ of hydrated water and/or –NH group [15]. The C=N stretching frequency is at 1593, 1592, 1596, and 1604 cm^{-1} for Co(II), Ni(II), Cu(II), and Zn(II) complexes, respectively. These values are lower than free azomethine group at 1614 cm^{-1}, indicating coordination through the azomethine nitrogen. The asymmetric vibrations of $–COO^-$ expected at 1600 cm^{-1}

Table 2. Analytical parameters of M(furfural-his) complexes.

Complex	Color	Decomposition pt. (°C)	MW (Calcd)	Yield %	Elements observed (Calcd)% M	C	H	N	Molar conductance (Ohm^{-1} $cm^{-2}\,mol^{-1}$)
$[Co(furfural\text{-}his)_2] \cdot 2H_2O$	Dark brown	> 260	567.25 (561.43)	78	10.43 (10.50)	46.92 (47.07)	4.78 (4.69)	15.01 (14.97)	6.2
$[Ni(furfural\text{-}his)_2] \cdot 2H_2O$	Dark purple	> 210	567.14 (561.19)	69	10.48 (10.46)	46.96 (47.89)	4.72 (4.67)	14.88 (14.98)	4.5
$[Cu(furfural\text{-}his)] \cdot NO_3$	Dark green	> 260	355.21 (358.8)	62	17.69 (17.56)	36.76 (36.82)	3.08 (3.17)	15.77 (15.61)	48.6
$[Zn(furfural\text{-}his)_2] \cdot 2H_2O$	Colorless	> 265	564.36 (567.88)	75	11.56 (11.51)	46.33 (46.53)	4.73 (4.62)	14.83 (14.80)	3.3

Table 3. Important IR spectral data of M(furfural-his) complexes.

Complex	$\nu_{N\text{–}H}$ and/or $\nu_{O\text{–}H}$ (cm^{-1})	$\nu_{C=N}$ and $\nu_{C=O}$ (cm^{-1})	ν_{CO} (cm^{-1})	ν_{NO_3} (cm^{-1})
[Co(furfural-his)$_2$] · 2H$_2$O	3400–3000(s)	1593(s)	1384(s)	–
[Ni(furfural-his)$_2$] · 2H$_2$O	3399–3000(s)	1592(s)	1384(s)	–
[Cu(furfural-his)] · NO$_3$	3449–3000(s)	1623(s)	1383(s)	1763(m)
[Zn(furfural-his)$_2$] · 2H$_2$O	3417–3000(s)	1604(s)	1384(s)	–

s – strong; m – medium.

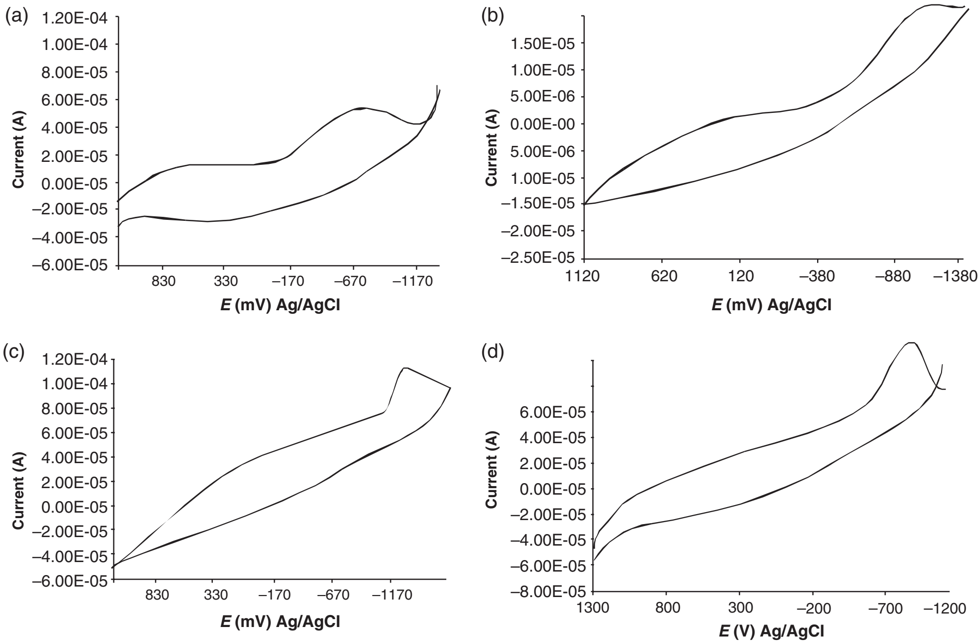

Figure 1. Cyclic voltammogram of (a) Co(II), (b) Ni(II), (c) Cu(II), and (d) Zn(II) complexes of furfural-his.

are merged with C=N vibration, while symmetric –COO$^-$ vibrations appeared at $\sim$1380 cm^{-1} for all the complexes. The difference between the two vibrations [$\Delta\nu_{(COO^-)} \sim 200\,cm^{-1}$] indicates unidenticity of the carboxylato [15].

In the Cu(II) complex, an additional band at 1762 cm^{-1} is due to –NO$_3$ [15]. The furan ring breathing for Cu(II) appears at 1013 cm^{-1}, lower than free ligand at 1026 cm^{-1}, suggesting coordination of furan oxygen. Thus, it is clear that furfural-his is coordinated through imino and imidazole nitrogens and carboxylato oxygen for [M(furfural-his)$_2$] · 2H$_2$O (M = Co(II), Ni(II), and Zn(II)) and tetradentate binding through furan and carboxylato oxygens and imino and imidazole nitrogens in [Cu(furfural-his)] · NO$_3$.

3.2.2. Cyclic voltammetric studies. Cyclic voltammograms for the complexes are given in figure 1. An irreversible reduction response is observed for Co(II) complex at −0.94 V for the one step, two electron Co(II) → Co(0) reduction [16]. Ni(II) complex

Table 4. Antibacterial activities of M(furfural-his) complexes (% inhibition).

	Concentration (μg)							
	E. coli				*S. aureus*			
Complex	**5**	**10**	**15**	**20**	**5**	**10**	**15**	**20**
[Co(furfural-his)$_2$] · 2H_2O	4	6	8	12	5	11	7	21
[Ni(furfural-his)$_2$] · 2H_2O	6	10	14	18	6	14	19	23
[Cu(furfural-his)] · NO_3	7	12	17	22	8	16	21	28
[Zn(furfural-his)$_2$] · 2H_2O	4	7	12	16	7	13	18	22

has a cathodic maximum at −1.1 V, due to irreversible Ni(II) → Ni(0) reduction. In Cu(II) complex, irreversible two-electron reduction takes place at −1.2 V. The Zn(II) complex shows reduction response at −0.90 V due to the Zn(II) → Zn(0) reduction [16].

3.3. *Antibacterial activity studies*

Antibacterial activities towards *E. coli* and *S. aureus* (table 4) increase with increase in concentration. Increased toxicity of complexes arises from Tweedy's chelation theory [17]. Furthermore, the mode of action of the compounds can involve formation of a hydrogen bond through >C=N group with the active centers of cell constituents resulting in interference with normal cell processes. Cu(II) complexes have higher activity compared to Co(II), Ni(II), and Zn(II) complexes.

Acknowledgements

We thank Dr M.A. Neelakandan, Department of Chemistry, National Engineering College, Kovilpatti – 628 503 and Dr S. Theodore David Manickam, Department of Chemistry, St. John's College, Tirunelveli – 627 002 for their help to carry out this work.

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