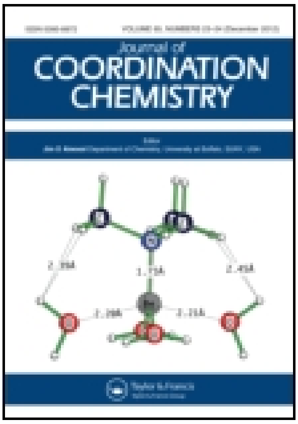
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:33
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Spectroscopic studies and determination of the formation constants and thermodynamic parameters for a new water-soluble Co(II) Schiff-base complex and some imidazole derivatives

Mehdi Ebrahimpour [a] & Mahdi Behzad [a]
[a] Department of Chemistry , College of Science, Semnan University , Semnan , Iran

Published online: 14 Apr 2011.

To cite this article: Mehdi Ebrahimpour & Mahdi Behzad (2011) Spectroscopic studies and determination of the formation constants and thermodynamic parameters for a new water-soluble Co(II) Schiff-base complex and some imidazole derivatives, Journal of Coordination Chemistry, 64:8, 1426-1435, DOI: 10.1080/00958972.2011.570756

To link to this article: http://dx.doi.org/10.1080/00958972.2011.570756

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Journal of Coordination Chemistry
Vol. 64, No. 8, 20 April 2011, 1426–1435

Spectroscopic studies and determination of the formation constants and thermodynamic parameters for a new water-soluble Co(II) Schiff-base complex and some imidazole derivatives

MEHDI EBRAHIMPOUR and MAHDI BEHZAD*

Department of Chemistry, College of Science, Semnan University, Semnan, Iran

(*Received 2 January 2011; in final form 21 February 2011*)

A new water-soluble Co(II) Schiff-base complex, sodium[{*N,N*′-bis(5-sulfosalicylidene)-1,8-diamino-3,6-dioxaoctan}cobalt] dihydrate, abbreviated as $Na_2[Co(II)L]$, was synthesized and characterized. The formation constants and thermodynamic parameters for the interaction of this complex with imidazole (Im) and 1-methylimidazole (MeIm) were determined spectroscopically in aqueous solution, ethanol/water (10/90), and methanol/water (10/90) under physiological conditions (pH = 7), constant ionic strength ($I = 0.1\ \mathrm{mol\,dm^{-3}}\ KNO_3$), and various temperatures ranging from 294 to 310 K. Our spectroscopic and thermodynamic results show that this adduct formation is endothermic and the positive values of ΔS_f° make ΔG_f° negative. The trend in variation of ΔH_f° and ΔS_f° for Im is in the order water > methanol > ethanol, but for MeIm it is in the opposite order which is related to the hydrogen bonding between solvents and these donors. Formation constants between MeIm and $Na_2[Co(II)L]$ in these three solvents are larger than for Im which depends on the electron donation of methyl on MeIm.

Keywords: Benesi–Hildebrand equation; Formation constant; Thermodynamic parameters; Co(II) Schiff base

1. Introduction

The cobalt complexes derived from tetradentate Schiff-base ligands have immense importance in biochemistry [1], magnetochemistry, and materials sciences. Some of these complexes mimic cobalamin (B_{12}) coenzymes [2–5]. The ability of certain cobalt(II) complexes to bind dioxygen reversibly, discovered decades ago [6], is being studied [7]. Cobalt(II) Schiff-base complexes are of considerable importance because of their catalytic activities in the synthesis of important compounds [8–10]. Cobalt complexes have also shown their role in the development of charge-transfer (CT) complexes. CT complexes are currently being widely studied [11–15] and a large part of the existing knowledge of non-covalent binding is based on the measurement of formation constants in such complexes. The challenge in this field exists in open

---

*Corresponding author. Email: mbehzad@semnan.ac.ir

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2011.570756

questions such as why transfer of electrons takes place or whether the mixed-stack organic CT complexes have columns of alternating donor and acceptor molecules, etc. [16–18]. The structural and electronic details of both donors and acceptors play critical roles in CT complex formation. In continuation of recent publications on this subject [19–26], herein we report the synthesis and characterization of a new Co(II) complex of a tetradentate Schiff-base ligand and spectroscopic and thermodynamic studies of its adduct formation with imidazole (Im) and 1-methylimidazole (MeIm) in three different solutions under physiological condition (pH = 7). The Schiff base is chosen to be sterically and electronically different from our previous reports to obtain better understanding about the factors affecting complex formation. The ionic strength was optimized to $I = 0.1\,\mathrm{mol\,dm^{-3}}$ KNO_3 and the formation constants and thermodynamic parameters were obtained at various temperatures by spectroscopic measurements.

2. Experimental

2.1. *Materials and instruments*

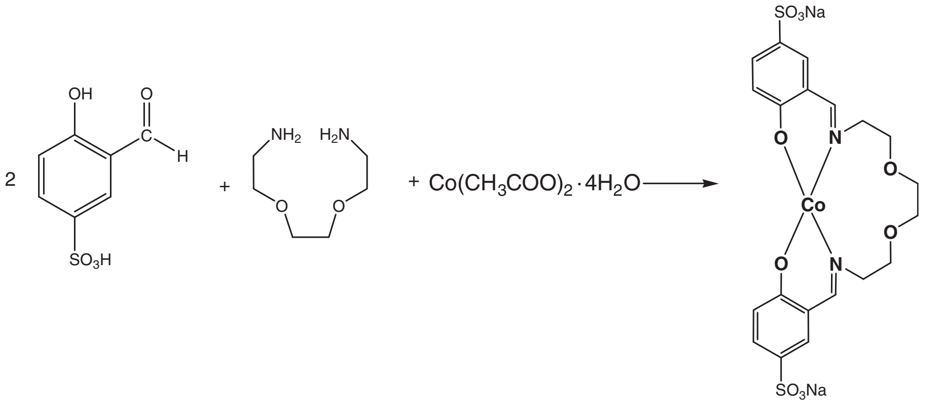
Imidazole (Im) and 1-methylimidazole (MeIm) were purchased from Biochemika, Fluka. 1,8-Diamino-3,6-dioxaoctan, 2-hydroxybenzaldehyde, ethanol, methanol, diethyl ether, and KNO_3 all were purchased from Merck. Doubly distilled, deionized water was used throughout. ^{1}H NMR spectra were recorded on a 500 MHz Bruker FT-NMR spectrometer in D_2O; chemical shifts (δ) are given in parts per million. IR spectra were obtained as KBr pellets using a Bruker FT-IR instrument. Elemental analyses (C, H, N) were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elemental-Analysesysteme, Gmbh, West Germany). UV-Vis spectra were recorded by a SHIMADZU UV-Vis 1650 pc spectrophotometer equipped with a water circulator and thermostatted multicell holder. A Metrohm 757 VA computrace instrument was employed to obtain a cyclic voltammogram.

2.2. *Synthesis of sodium salicylaldehyde-5-sulfonate monohydrate (L)*

Sodium salicylaldehyde-5-sulfonate was prepared following the literature method [27, 28]. ^{1}H NMR and other physical properties reported were used to confirm the synthesis and purity of the product. ^{1}H NMR: 9.86 (CHO, 1H, s), 8.02 (C–H_{Ar}, 1H, d), 7.85 (C–H_{Ar}, 1H, dd), 6.97 (C–H_{Ar}, 1H, d). Selected IR: 1667 cm^{-1} (CHO).

2.3. *Synthesis of sodium[{N,N′-bis(5-sulfosalicylidene)-1,8-diamino-3,6-dioxaoctan}-cobalt] dihydrate ($Na_2[Co(II)L]$)*

To a solution of sodium salicylaldehyde-5-sulfonate (9.0 mmol, 1.23 g) in water (9 mL) were added 1,8-diamino-3,6-dioxaoctan (4.5 mmol, 0.67 g) and $Co(CH_3COO)_2{\cdot}4H_2O$ (4.5 mmol, 1.12 g). The mixture was stirred under a nitrogen atmosphere for 2 h. The product was obtained as a brown precipitate, which was filtered off under nitrogen and washed successively with ethanol and diethyl ether and dried by passage of nitrogen at room temperature. Recrystallization from ethanol gave 1.26 g (49%) of analytically



Scheme 1. Reaction pathway for the synthesis of $Na_2[Co(II)L]$.

pure complex which was dried by passage of N_2. Selected IR data: 1626 cm^{-1} (HC=N), 1183, 1038, and 603 cm^{-1} (SO_3^-), 1114 cm^{-1} (C–O–C). Anal. Calcd for $C_{20}H_{24}N_2Na_2O_{12}S_2$ (%): C, 41.48; H, 4.18; N, 4.88. Found (%): C, 41.32; H, 4.11; N, 5.01.

3. Results and discussion

3.1. *Syntheses*

The water-soluble Co(II) complex was prepared by a template method as shown in scheme 1. In the IR spectrum of the complex, the presence of a sharp band at 1626 cm^{-1} is indicative of the formation of the azomethine (CH=N) group. The peak at 1667 cm^{-1} of sodium salicylaldehyde-5-sulfonate vanished showing that the carbonyl is converted to an iminic group. In mononuclear complexes derived from such ligands, the metal exists in the outer N_2O_2 coordination sphere [29, 30]. IR spectroscopy is important in supporting this coordination mode. The ν(C–O–C) in such ligands and complexes appears at 1115 cm^{-1}; in our complex, ν(C–O–C) appears at 1114 cm^{-1} indicating that Co(II) is not coordinated to the inner oxygens, but is coordinated to the outer N_2O_2 [31]. In the UV-Vis spectrum an intense band at 313 nm is due to the $\pi \rightarrow \pi^*$ intraligand transition. Elemental analyses are consistent with the proposed complex.

3.2. *Electrochemistry*

The electrochemical behavior of 10^{-3} mol L^{-1} solution of the tetradentate Co(II) Schiff-base complex was studied by cyclic voltammetry in aqueous solution containing 0.1 mol L^{-1} KCl as supporting electrolyte from −2 to +1 V. A working Pt electrode, an auxillary Pt electrode, and a reference Ag/AgCl electrode were employed for this electrochemical study. The complex shows an irreversible peak at –0.56 V due to Co^{II}/Co^{I}.

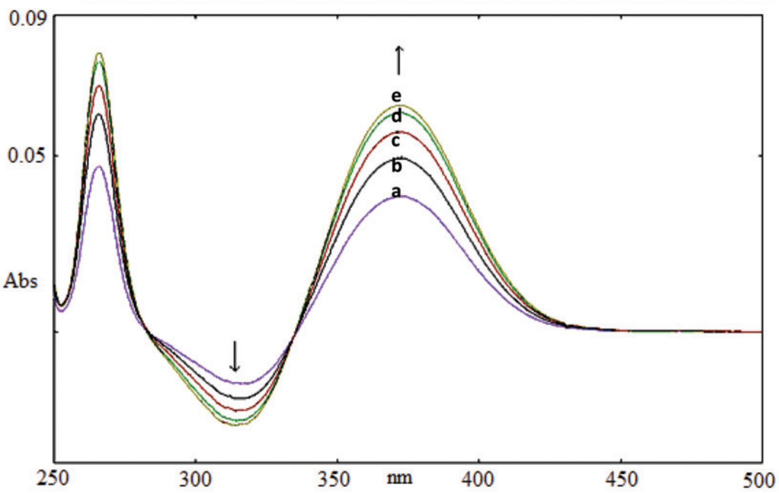


Figure 1. UV-Vis absorption spectra obtained for the mixtures containing $Na_2[Co(II)L]$ (3×10^{-5} mol dm^{-3}) and MeIm (a) 0.54×10^{-4} (b) 1.08×10^{-4} (c) 1.62×10^{-4} (d) 2.16×10^{-4} and (e) 2.70×10^{-4} mol L^{-1}; all taken against pristine solution as reference in ethanolic solution ($I = 0.1$ mol dm^{-3} KNO_3, $T = 310$ K).

3.3. *Electronic spectroscopic studies of the interaction of $Na_2[Co(II)L]$ with Im and MeIm*

Complex formation between the water-soluble Co(II) complex and imidazole or 1-methylimidazole was studied spectroscopically by following the spectral changes due to stepwise addition of imidazole or 1-methylimidazole to a fixed concentration of $Na_2[Co(II)L]$ (3×10^{-5} mol dm^{-3}) in three different media. The experiments were performed in water, water/methanol (90/10), and water/ethanol (90/10) solutions at temperatures ranging from 294 to 310 K, and at constant ionic strength ($I = 0.1$ mol dm^{-3} KNO_3) and pH = 7, against the pristine acceptor solutions as reference for subtracting its absorbance. Figure 1 shows a sample spectral variation for the interaction of the complex with MeIm in ethanolic solution with the described conditions. By molecular complex formation between the water-soluble Schiff-base complex (as acceptor) and imidazole derivative (as donor) with increase in concentration of the donor, a new charge CT peak appeared at 370 nm with gradually increasing intensity. This molecular complex has different absorption from the acceptor, while the donor does not have absorption in that area. All calculations are done at this wavelength.

3.4. *Determination of formation constants and interpretation of thermodynamic parameters*

The Benesi–Hildebrand (B–H) equation (equation 1) [32] (for cells with 1 cm optical length) is usually employed for calculation of the formation constants of complexes with 1 : 1 (donor : acceptor) stoichiometry:

$$\frac{[A]_0[D]_0}{A - A_A^0 - A_D^0} = \frac{[D]_0}{\varepsilon'} + \frac{1}{\varepsilon' K}, \tag{1}$$

Table 1. Absorbance data for the spectrophotometric determination of the stoichiometry, formation constant, and corrected molar absorptivity of $Na_2[Co(II)L]$–Im complex in aqueous solution ($I = 0.1\ mol\ dm^{-3}\ KNO_3$) and pH 7.0 against pristine solution as reference.

T (K)	10^4 $[D]_0$ ($mol\ dm^{-3}$)	10^5 $[A]_0$ ($mol\ dm^{-3}$)	A	ε' ($dm^3\ mol^{-1}\ cm^{-1}$)	K ($dm^3\ mol^{-1}$)	ln$K$
294	0.54	3	0.025	2960	8165	9.00
	1.08		0.044			
	1.62		0.053			
	2.16		0.056			
	2.70		0.060			
298	0.54	3	0.038	3249	12,614	9.44
	1.08		0.058			
	1.62		0.066			
	2.16		0.071			
	2.70		0.075			
302	0.54	3	0.043	3249	14,057	9.55
	1.08		0.060			
	1.62		0.067			
	2.16		0.072			
	2.70		0.078			
306	0.54	3	0.048	3555	14,904	9.61
	1.08		0.065			
	1.62		0.075			
	2.16		0.082			
	2.70		0.085			
310	0.54	3	0.056	4020	15,915	9.68
	1.08		0.075			
	1.62		0.086			
	2.16		0.094			
	2.70		0.097			

here $[A]_0$ and $[D]_0$ are the initial concentrations of the acceptor and donor ($mol\ cm^{-1}$), respectively. A is the absorbance of the mixture at λ_{CT} and A_A^0 and A_D^0 are the absorbance of the acceptor and donor at this λ. ϵ' is equal to $\varepsilon_C - \varepsilon_A - \varepsilon_D$, the molar absorptivity of the complex, and ε_A and ε_D are those of the acceptor and donor, respectively. K is the formation constant of the complex. Equation (1) is valid if $[D]_0 >> [A]_0$. The plot of $[A]_0[D]_0/(A - A_A^0 - A_D^0)$ *versus* $[D]_0$ produces a straight line only if the 1 : 1 molecular complex is formed. In the case of 1 : 2 or mixture of 1 : 1 and 1 : 2 complex formation, a curve would be obtained and other equations are necessary to calculate K [33, 34]. Tables 1–3 show the absorbance data, the concentrations of Im and the calculated formation constants in the three solvents. Tables 4–6 show these data for the interactions with MeIm. The K measurements were repeated at least two times and were reproducible. From tables 1–6, it is obvious that the formation constants between MeIm and the acceptor complex are much greater than those of Im, suggesting that the electronic effect of the methyl group is dominant compared to its steric effect. Figure 2 shows linear plots of M against $[D]_0$ for titration of $Na_2[Co(II)L]$ with MeIm in aqueous solution at various temperatures ($T = 294$–310 K), where M is $[A]_0[D]_0/(A - A_A^0 - A_D^0)$. These plots signify that only 1 : 1 adduct is formed. Similar plots are obtained for the other systems.

The thermodynamic parameters of the studied systems were calculated by using the van't Hoff equation (equation 2).

$$\mathrm{LnK} = \frac{-\Delta H^o}{\mathrm{RT}} + \frac{\Delta S^o}{\mathrm{R}}. \tag{2}$$

Table 2. Absorbance data for the spectrophotometric determination of the stoichiometry, formation constant, and corrected molar absorptivity of $Na_2[Co(II)L]$–Im complex in methanolic solution ($I = 0.1$ mol dm^{-3} KNO_3) and pH 7.0 against pristine solution as reference.

T (K)	10^4 $[D]_0$ (mol dm^{-3})	10^5 $[A]_0$ (mol dm^{-3})	A	ε' (dm^3 mol^{-1} cm^{-1})	K (dm^3 mol^{-1})	ln$K$
294	0.54	3	0.031	2639	11,695	9.37
	1.08		0.043			
	1.62		0.052			
	2.16		0.057			
	2.70		0.060			
298	0.54	3	0.032	2648	12,221	9.41
	1.08		0.045			
	1.62		0.052			
	2.16		0.058			
	2.70		0.061			
302	0.54	3	0.033	2677	13,107	9.48
	1.08		0.047			
	1.62		0.056			
	2.16		0.058			
	2.70		0.063			
306	0.54	3	0.036	2723	13,652	9.52
	1.08		0.047			
	1.62		0.057			
	2.16		0.060			
	2.70		0.065			
310	0.54	3	0.038	2767	14,062	9.59
	1.08		0.048			
	1.62		0.058			
	2.16		0.061			
	2.70		0.067			

Table 3. Absorbance data for the spectrophotometric determination of the stoichiometry, formation constant and corrected molar absorptivity of $Na_2[Co(II)L]$–Im complex in ethanolic solution ($I = 0.1$ mol dm^{-3} KNO_3) and pH 7.0 against pristine solution as reference.

T (K)	10^4 $[D]_0$ (mol dm^{-3})	10^5 $[A]_0$ (mol dm^{-3})	A	ε' (dm^3 mol^{-1} cm^{-1})	K (dm^3 mol^{-1})	ln$K$
294	0.54	3	0.032	2730	11,482	9.35
	1.08		0.045			
	1.62		0.052			
	2.16		0.059			
	2.70		0.062			
298	0.54	3	0.034	2742	12,532	9.44
	1.08		0.047			
	1.62		0.054			
	2.16		0.060			
	2.70		0.064			
302	0.54	3	0.037	2863	12,841	9.46
	1.08		0.050			
	1.62		0.055			
	2.16		0.063			
	2.70		0.068			
306	0.54	3	0.037	3021	13,510	9.51
	1.08		0.054			
	1.62		0.061			
	2.16		0.067			
	2.70		0.072			
310	0.54	3	0.040	3506	13,712	9.53
	1.08		0.062			
	1.62		0.073			
	2.16		0.078			
	2.70		0.083			

Table 4. Absorbance data for the spectrophotometric determination of the stoichiometry, formation constant and corrected molar absorptivity of $Na_2[Co(II)L]$–MeIm complex in aqueous solution ($I = 0.1\ mol\,dm^{-3}$ KNO_3) and pH 7.0 against pristine solution as reference.

T (K)	10^4 $[D]_0$ ($mol\,dm^{-3}$)	10^5 $[A]_0$ ($mol\,dm^{-3}$)	A	ε' ($dm^3\,mol^{-1}\,cm^{-1}$)	K ($dm^3\,mol^{-1}$)	ln$K$
294	0.54	3	0.038	2491	15,316	9.64
	1.08		0.058			
	1.62		0.063			
	2.16		0.067			
	2.70		0.071			
298	0.54	3	0.043	2990	17,789	9.77
	1.08		0.060			
	1.62		0.067			
	2.16		0.071			
	2.70		0.074			
302	0.54	3	0.047	3091	18,486	9.82
	1.08		0.061			
	1.62		0.069			
	2.16		0.075			
	2.70		0.077			
306	0.54	3	0.051	3204	20,339	9.92
	1.08		0.067			
	1.62		0.075			
	2.16		0.078			
	2.70		0.081			
310	0.54	3	0.057	3543	21,711	9.98
	1.08		0.075			
	1.62		0.083			
	2.16		0.087			
	2.70		0.091			

Table 5. Absorbance data for the spectrophotometric determination of the stoichiometry, formation constant and corrected molar absorptivity of $Na_2[Co(II)L]$–MeIm complex in methanolic solution ($I = 0.1$ mol dm^{-3} KNO_3) and pH 7.0 against pristine solution as reference.

T (K)	10^4 $[D]_0$ ($mol\,dm^{-3}$)	10^5 $[A]_0$ ($mol\,dm^{-3}$)	A	ε' ($dm^3\,mol^{-1}\,cm^{-1}$)	K ($dm^3\,mol^{-1}$)	ln$K$
294	0.54	3	0.028	2452	10,592	9.27
	1.08		0.039			
	1.62		0.045			
	2.16		0.050			
	2.70		0.056			
298	0.54	3	0.032	2780	11,717	9.37
	1.08		0.045			
	1.62		0.056			
	2.16		0.059			
	2.70		0.063			
302	0.54	3	0.036	2889	12,451	9.44
	1.08		0.048			
	1.62		0.057			
	2.16		0.065			
	2.70		0.066			
306	0.54	3	0.037	2933	14,265	9.56
	1.08		0.054			
	1.62		0.062			
	2.16		0.067			
	2.70		0.069			
310	0.54	3	0.038	2965	16,214	9.69
	1.08		0.058			
	1.62		0.068			
	2.16		0.069			
	2.70		0.071			

Table 6. Absorbance data for the spectrophotometric determination of the stoichiometry, formation constant and corrected molar absorptivity of $Na_2[Co(II)L]$–MeIm complex in ethanolic solution ($I = 0.1\,mol\,dm^{-3}$ KNO_3) and pH 7.0 against pristine solution as reference.

T (K)	10^4 $[D]_0$ (mol dm^{-3})	10^5 $[A]_0$ (mol dm^{-3})	A	ε' (dm^3 mol^{-1} cm^{-1})	K (dm^3 mol^{-1})	ln$K$
294	0.54	3	0.021	1740	14,774	9.60
	1.08		0.035			
	1.62		0.037			
	2.16		0.040			
	2.70		0.041			
298	0.54	3	0.029	2020	16,125	9.69
	1.08		0.039			
	1.62		0.042			
	2.16		0.047			
	2.70		0.050			
302	0.54	3	0.038	2316	18,772	9.84
	1.08		0.045			
	1.62		0.050			
	2.16		0.056			
	2.70		0.059			
306	0.54	3	0.038	2489	21,600	9.98
	1.08		0.055			
	1.62		0.059			
	2.16		0.060			
	2.70		0.064			
310	0.54	3	0.044	2498	22,875	10.04
	1.08		0.052			
	1.62		0.057			
	2.16		0.063			
	2.70		0.065			

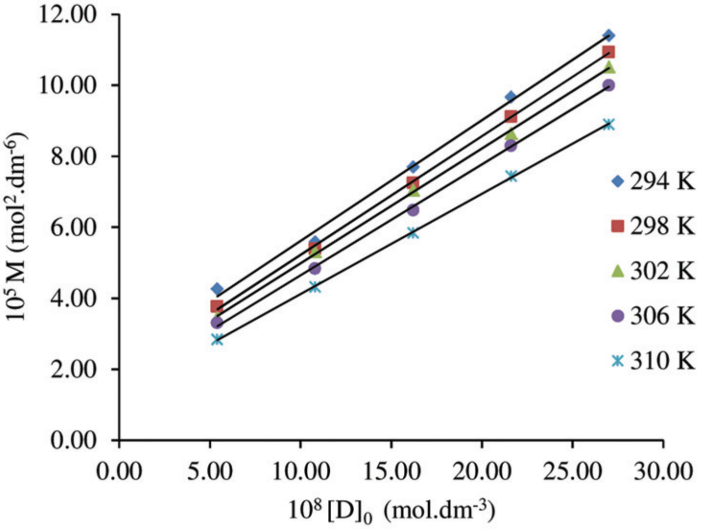


Figure 2. Typical plots of M against $[D]_0$ for $Na_2[Co(II)L]$ with MeIm in aqueous solution at various temperatures ($T = 294$–$310\,K$).

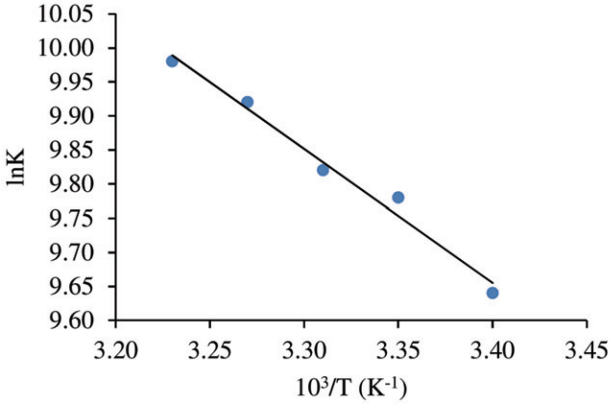


Figure 3. Plot of ln K against $1/T$ for $Na_2[Co(II)L]$ with MeIm in aqueous solution.

Table 7. The thermodynamic parameter values ΔH_f°, ΔS_f°, and ΔG_f° for $Na_2[Co(II)L]$ with Im and MeIm.

				ΔG_f° (kJ mol^{-1})				
Solvent	Donor	ΔH_f° (kJ mol^{-1})	ΔS_f° (J mol^{-1} K^{-1})	294 K	298 K	302 K	306 K	310 K
W	Im	15.0 ± 1.2	128.0 ± 8.8	−22.7 ± 1.7	−23.2 ± 1.6	−23.7 ± 2.3	−24.2 ± 2.9	−24.7 ± 2.8
M/W	Im	9.4 ± 0.9	109.8 ± 10.4	−22.9 ± 1.9	−23.3 ± 2.2	−23.5 ± 1.3	−24.2 ± 3.4	−24.6 ± 2.2
E/W	Im	8.6 ± 0.8	107.8 ± 10.2	−22.8 ± 1.8	−23.3 ± 1.9	−23.7 ± 4.1	−24.1 ± 3.9	−24.6 ± 2.8
W	MeIm	16.3 ± 2.2	135.7 ± 14.6	−23.6 ± 2.8	−24.1 ± 2.3	−24.7 ± 4.5	−25.2 ± 2.8	−25.7 ± 2.8
M/W	MeIm	20.6 ± 1.8	146.8 ± 14.2	−22.6 ± 2.8	−23.2 ± 1.6	−23.7 ± 4.3	−24.3 ± 3.0	−24.9 ± 3.9
E/W	MeIm	23.0 ± 2.1	157.9 ± 14.7	−23.4 ± 2.5	−24.0 ± 1.9	−24.7 ± 2.0	−25.3 ± 4.6	−25.9 ± 5.4

W: water; M: methanol; E: ethanol

Figure 3 shows a typical plot of ln$K$ *versus* $1/T$ for $Na_2[Co(II)L]$ with MeIm in aqueous solution. The thermodynamic parameters are collected in table 7.

Compared to the previous studies [19, 20], the acceptor property of this Schiff-base complex is altered by both steric and electronic factors. The steric factor obviously disfavors complex formation but electronic factors could favor it. The value of ΔH_f° and its sign depend on two factors. One is the heat of bond formation which must be negative while the other is the positive solvation parameter [20]. The electronic effect in the acceptor complex is due to the presence of two oxygens in the diamine of the Schiff-base ligand. In hydrogen-bonding solvents, the initial Schiff-base complex and the resulting adduct are both subject to hydrogen bonding which affects the value of ΔH_f°. The positive values of ΔH_f° (table 7) indicate that the solvation factor is dominant. The trend in variations of ΔH_f° is in the order water > methanol > ethanol, rationalized that imidazole is more solvated in water consistent with more hydrogen-bonding ability of water. On the other hand, the presence of methyl on 1-methylimidazole makes this molecule less soluble in water and with less hydrogen bonding, consistent with the observed trend of ΔH_f° for MeIm. The trend for variations of ΔS_f° is also consistent with this; the value and the sign of ΔS_f° are dependent on the nature of solvation which makes its values positive. The values of the obtained thermodynamic parameters are in reasonable agreement with the previously studied cobalamins and the complex is therefore a model for the study of the cobalamin system [35]. The values of ΔH_f° and ΔS_f° are both shifted to more negative values compared to previous report [19], confirming that the starting acceptor complex is more subjected to hydrogen bonding.

Acknowledgments

We would like to acknowledge financial support from the office of gifted students at Semnan University. We are also grateful to Dr N. Azizi and Mr Reza Valiollahi for their kind support and help during this work.

References

[1] N. Shahabadi, S. Kashanian, F. Darabi. *Eur. J. Med. Chem.*, **45**, 4239 (2010).
[2] A. Bottcher, T. Takeuchi, M.I. Simon, T.J. Meade, H.B. Gray. *J. Inorg. Biochem.*, **59**, 221 (1995).
[3] P.A. Schwartz, P.A. Frey. *Biochemistry*, **46**, 7284 (2007).
[4] C.G. Riordan. *Compr. Coord. Chem. II*, **8**, 677 (2004).
[5] K.P. Jensen, U. Ryde. *J. Am. Chem. Soc.*, **127**, 9117 (2005).
[6] A. Werner, A. Mylius. *Z. Anorg. Allg. Chem.*, **16**, 245 (1898).
[7] E.V. Rybak-Akimova, W. Otto, P. Deardorf, R. Roesner, D.H. Busch. *Inorg. Chem.*, **36**, 2746 (1997).
[8] S. Förster, A. Rieker, K. Maruyama, K. Murata, A. Nishinaga. *J. Org. Chem.*, **61**, 3320 (1996).
[9] K.C. Gupta, H.K. Abdulkadir, S. Chand. *J. Mol. Catal. A: Chem.*, **202**, 253 (2003).
[10] A. Caselli, M.G. Buonomenna, F. de Baldironi, L. Laera, S. Fantauzzi, F. Ragaini, E. Gallo, G. Golemme, S. Cenini, E. Drioli. *J. Mol. Catal. A: Chem.*, **317**, 72 (2010).
[11] J. Kang, J.A. Nelson, M. Lu, B. Xie, Z. Peng, D.R. Powell. *Inorg. Chem.*, **43**, 6408 (2004).
[12] H. Nakanishi, H. Morita, S. Nagakura. *J. Mol. Spectrosc.*, **65**, 295 (1977).
[13] J.W. Verhoeven, I.P. Dirkx, Th.J. de Boer. *J. Mol. Spectrosc.*, **42**, 149 (1972).
[14] K. Gonther. *Inorg. Chem. Commun.*, **4**, 160 (2001).
[15] M. Asadi, A.H. Kianfar, S. Torabi, K. Mohammadi. *J. Chem. Thermodyn.*, **40**, 523 (2008).
[16] R.S. Mulliken, W.B. Person. *Molecular Complexes*, Wiley, New York (1969).
[17] D.J. Raber, J.M. Harris, P.R. Schleyer. In *Ions and Ion Pairs in Organic Reactions*, M. Swartz (Ed.), Wiley, New York (1974).
[18] M. Chanon, M.D. Hawley, M.A. Fox. In *Photoinduced Electron Transfer*, M.A. Fox, M. Chanon (Eds.), Elsevier, Amsterdam (1988).
[19] D.M. Boghaei, E. Askarizadeh, A. Bezaatpour. *Spectrochim. Acta A*, **69**, 624 (2008).
[20] D.M. Boghaei, M. Gharagozlou. *Spectrochim. Acta A*, **63**, 139 (2006).
[21] M.M. Najafpour, D.M. Boghaei, P.J.R. Sjöberg. *Spectrochim. Acta A*, **75**, 1168 (2010).
[22] D.M. Boghaei, M. Gharagozlou. *Spectrochim. Acta A*, **67**, 944 (2007).
[23] S. Baniyaghoob, M.M. Najafpour, D.M. Boghaei. *Spectrochim. Acta A*, **75**, 970 (2010).
[24] D.M. Boghaei, S. Farvid, M. Gharagozlou. *Spectrochim. Acta A*, **66**, 650 (2007).
[25] M. Gharagozlou, D.M. Boghaei. *Spectrochim. Acta A*, **71**, 1617 (2008).
[26] D.M. Boghaei, M. Gharagozlou. *Spectrochim. Acta A*, **61**, 3061 (2005).
[27] M. Botsivali, D.F. Evans, P.H. Misse, M.W. Upton. *J. Chem. Soc., Dalton Trans.*, 1147 (1985).
[28] K.J. Berry, F. Moya, K.S. Murray, A.M.B. Van Den Bergen, B.O. West. *J. Chem. Soc., Dalton Trans.*, 109 (1982).
[29] T. Yu, W. Su, W. Li, Z. Hong, R. Hua, M. Li, B. Chu, B. Li, Z. Zhang, Z.Z. Hu. *Inorg. Chim. Acta*, **359**, 2246 (2006).
[30] H.J. Banbery, F. McQuillan, T.A. Hamor, C.J. Jones, J.A. McCleverty. *J. Chem. Soc., Dalton Trans.*, 1405 (1989).
[31] A.T. Vallina, H. Stoeckli-Evans. *Polyhedron*, **21**, 1177 (2002).
[32] H.A. Benesi, J.H. Hildebrand. *J. Am. Chem. Soc.*, **71**, 2703 (1949).
[33] A. Saha, A.K. Mukherjee. *Spectrochim. Acta A*, **60**, 1731 (2004).
[34] E.B. Fleischer, S. Jacobs, L. Mestichelli. *J. Am. Chem. Soc.*, **90**, 2527 (1968).
[35] K.L. Brown, G.-W. Wu. *Inorg. Chem.*, **33**, 4122 (1994).