

STABILITY AND MOLECULAR MODELLING OF COBALT(II) AND NICKEL(II) WITH POLYDENTATE SCHIFF BASE

Achour TERBOUCHE,^{a,b} Safia DJEBBAR,^{b,*} Ouassini BENALI-BAITICH,^b Mustayeen KHAN^c
and Gilles BOUET^c

^aCentre de Recherche Scientifique et Technique en Analyses Physico-Chimiques, BP 248 RP 16004, Alger, Algérie

^bLaboratoire d'Hydrometallurgie et Chimie Inorganique Moléculaire, USTHB, BP 32 Al Alia Alger, Algérie

^cLaboratoire de Chimie de Coordination, Faculté de Pharmacie 16 Boulevard Daviers, F-49100 Angers, France

Received May 3, 2007

The cobalt (II) and nickel (II) complexes with H₃L polydentate Schiff base (N[(1E) phenylmethylene N{2[2(2 {hydroxyphenylmethylene] amino} ethyl) imidazolidin -1-yl} ethylamine) were identified in water-ethanol medium (90%/10%) at 25°C at a constant ionic strength of 0.2 M by potentiometry. Sirko program was used in order to determine the number and the stability constants of the complex species formed in aqueous solution. Totally deprotonated species [ML] and protonated mononuclear species [MHL] (L= deprotonated polydentate ligand) were found in the Co(II)-H₃L and Ni(II)-H₃L systems. This study is completed by molecular modelling. The minimized steric energy and optimized geometry of Co(II) and Ni(II) complexes were obtained using the computer EMO program. Indeed a direct correlation was obtained between steric energies of the complexes and their formation constants.

INTRODUCTION

Schiff base ligands have gained importance because of physiological and pharmacological activities associated with them. They constitute an interesting class of chelating agents capable of coordinating metal ions giving complexes which serve as models for biological systems.^{1,2}

Recently, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing oxygen, nitrogen and other donors.³⁻¹³ This may be attributed to their stability, biological activity and potential applications in many fields, such as oxidation catalysis and electrochemistry.¹⁴⁻¹⁶

In this paper, we report the protonation properties of the N[(1E) phenylmethylene N{2[2(2 {hydroxyphenylmethylene] amino} ethyl) imidazolidin -1-yl} ethylamine Schiff base (Fig. 1) and we present the results of complexation of the this ligand with cobalt(II) and nickel(II) in water ethanol medium at 298 K and at a constant ionic strength (0.2 M). Here, we set out to investigate, by potentiometric and molecular modelling means, the coordinating ability of Schiff base ligand with metal ions. The complex species were identified potentiometrically and their respective formation constants were calculated by Sirko program.¹⁷ The Co(II) and Ni(II) complexes formed were modeled by molecular mechanics.

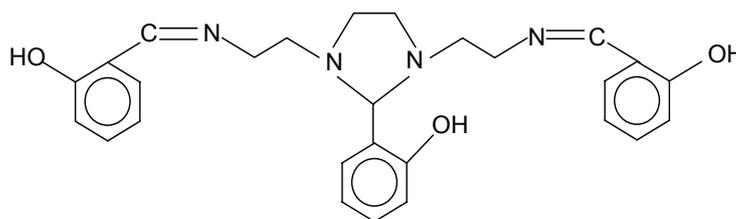


Fig. 1 – Ligand structure.

*Corresponding author: safia.djebbar@netcourrier.com

RESULTS AND DISCUSSION

1. Acid-base properties of the ligand

The fully protonated species is designed as H_3L^{2+} and the fully deprotonated species is L^{3-} . The ligand, in his neutral form (H_3L), has only three labile protons due to the phenolic groups. From the fitting analysis of potentiometric titration curve of the H_3L (Fig. 2) using Sirko program, five protonation constants were determined which are defined by equation:



Based on chemical evidences, the first three protonation constants of the ligand ($\log K_i^H = 10.64, 10.43, 8.77$) are attributed to the phenolic

groups. The two remaining $\log K_i^H$ values (6.49, 3.81) of the ligand are attributed to the protonated imine groups.

The results obtained by Sirko program are in good agreement with the protonation constants calculated by Irving-Rossotti method (Table 1).

2. Complexation studies

The complexation properties of the ligand toward the Co^{2+} and Ni^{2+} ions were studied by potentiometry. The titration curves obtained for mixtures of the polydentate Schiff base and metal ions in a 1:1 ratio are depicted in Fig. 2.

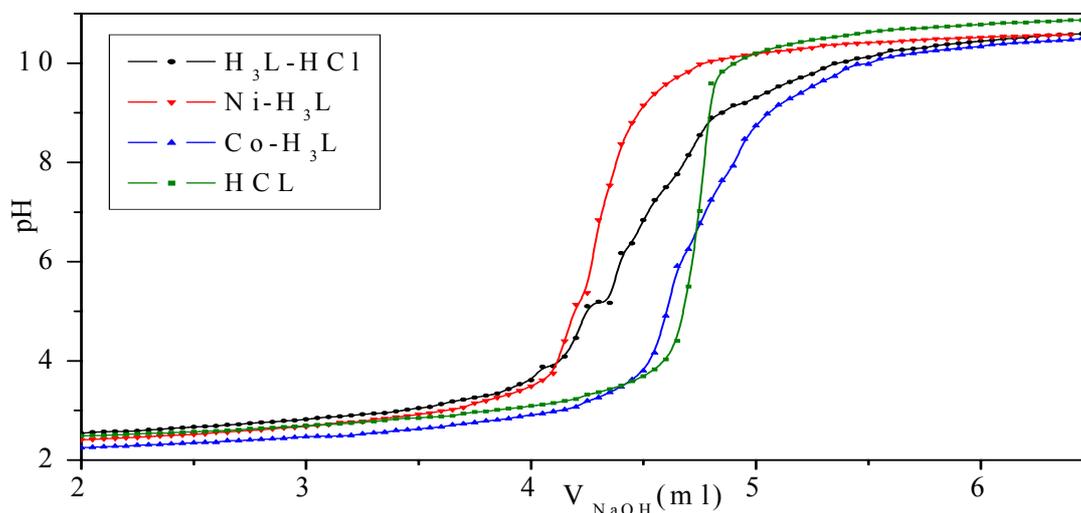


Fig. 2 – Potentiometric titration curves $[M]=[H_3L]=10^{-3}$ M, $I=0.2$ M at $T=25 \pm 0.1$ °C.

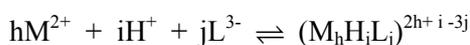
Table 1

Logarithm of protonation constants ($\log K_i^H$) and stability constants ($\log \beta_{hij}$)

Species		H ₃ L	Co-H ₃ L	Ni-H ₃ L
		Sirko	Irving Rossotti	
$[H_4L]^+ / [H_5L]^{2+}$	$\log K_5$	3.81(0.09)	2.44	
$[H_3L] / [H_4L]^+$	$\log K_4$	6.49(0.04)	5.69	
$[H_2L] / [H_3L]$	$\log K_3$	8.77(0.04)	8.04	
$[HL]^{2-} / [H_2L]^-$	$\log K_2$	10.43(0.05)	10.40	
$[L^{3-}] / [HL]^{2-}$	$\log K_1$	10.64(0.03)	10.65	
	R%	1.11		
	R _{lim} %	0.3		
$[ML]$	$\log \beta_{101}$		9.07(0.07)	7.02(0.09)
$[MHL]$	$\log \beta_{111}$	-	15.08(0.06)	12.58(0.08)
	R%		1.46	1.11
	R _{lim} %		0.16	0.14

R%: reliability factor; R_{lim}%: limit reliability factor

Analysis of the curves shows that the metal complexation of the ligand starts at a quite lower pH (approximately 2.6 and 2.8 respectively for cobalt(II) and nickel(II)) indicating a strong interaction with cobalt(II). The Co(II)-H₃L and Ni(II)-H₃L curves shift to lower pH as compared to the corresponding ligand curve. This is due to a release of protons on coordination. The titration curves present two inflection points for cobalt (II)-H₃L and nickel (II)-H₃L systems. The protonated species [MHL] were formed at the acid pH range and [ML]⁻ species were formed at the basic pH range. The Sirko program gave convergence for models containing the [MH_iL]ⁱ⁻¹ species (i=0, 1), where the L is used for the ligand bearing three negative charges. The stability constants (β_{hij}) are defined by equation:



The comparison between the formation constants calculated for the complexes with H₃L (Table 1) shows that $\log\beta_{[ML]^-}$ is higher for Co(II) than the Ni(II) by a factor of approximately 2.05 logarithmic units. This indicates that the cobalt(II)

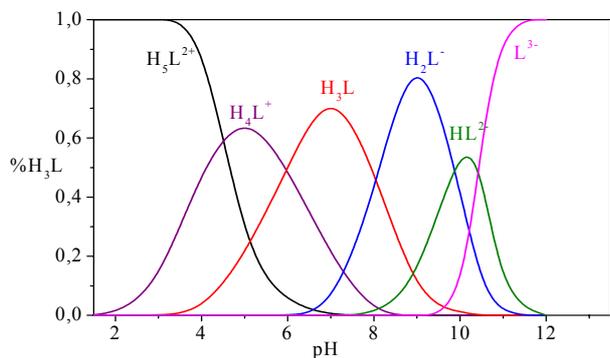


Fig. 3 – Species distributions curves of the H₃L ligand.

4. Molecular modelling

The ligand binds the nickel and cobalt ions through multidentate coordination mode with N_{azomethine}; imidazolidine and O_{hydroxyl}; water donor atoms. Only coordination 4, 5 and 6 around the central atom have been considered. The values of minimized steric energy of the complexes (Tables 2, 3) show that the 101 complexes are more stable than the 111 ones and the more stable complexes are formed when the ligand binds the metal in tetradentate (N_{azomethine}, O_{hydroxyl}) manner.

complexes are more stable than those formed with nickel(II).

3. Species distributions

As the pH increases, the ligand loses its protons to become H₅L²⁺, H₄L⁺, H₃L, H₂L⁻, HL²⁻ and L³⁻. The neutral H₃L ligand reaches its maximum concentration at pH=7 (70%) (Fig. 3).

On the basis of the potentiometric data and the equilibrium constants, curves of concentration distribution of Co(II) and Ni(II) were obtained. The first inflexion on the species distribution curve of the Co(II)-H₃L system (Fig.4) appears at pH=5.8, revealing that a monoprotection mononuclear chelate [CoHL] is formed in an appreciable concentration (maximum 72% at pH=6.9). The [CoL]⁻ complex becomes the predominant component from pH=8 to 10 and the maximum formation (100%) occurs at pH=9.2.

The [NiHL] protonated species begins to form pH=3.5 and its maximum formation occurs at pH= 6.0 (40%). The maximum formation (100%) of [NiL]⁻ deprotonated complex occurs at pH= 8.6.

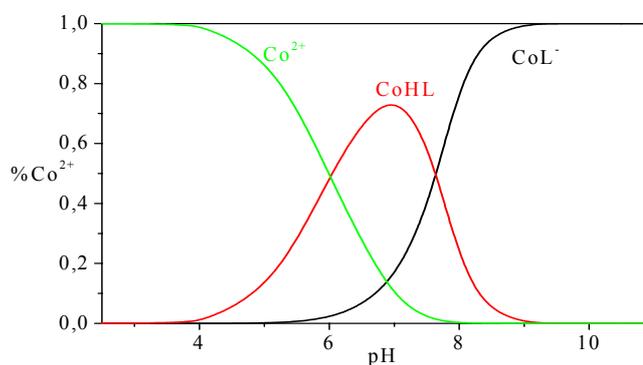
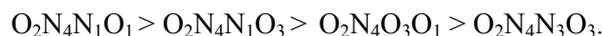


Fig. 4 – Species distributions curves of the Co(II)-H₃L system.

a. Tetradentate coordination mode

In coordination 6 (Table 2) the cobalt complexes are more stable than the nickel complexes and they are less stable in coordination 4. The stability order of Ni-H₃L and Co-H₃L complexes in coordination 4 is:



b. Pentadentate coordination mode

In coordination 5 (Table 3) the ligand favours the square pyramid form for the cobalt complexes and trigonal bipyramid geometry around the nickel ion.

Table 2

Steric energies (KJ/mol) of nickel and cobalt complexes in tetradentate coordination mode

Species	Coordination 4				Coordination 6
	O ₂ N ₄ N ₁ O ₁	O ₂ N ₄ N ₁ O ₃	O ₂ N ₄ O ₃ O ₁	O ₂ N ₄ N ₃ O ₃	
Ni-H ₃ L (101)	186.882	246.080	248.115	422.321	280.192
(111)	192.560	253.20	252.68	500.120	283.203
Co-H ₃ L (101)	195.987	230.801	250.615	412.085	163.308
(111)	205.441	249.846	264.585	483.654	179.240

Table 3

Steric energies (KJ/mol) of nickel and cobalt complexes in pentadentate coordination mode

Species	Coordination 5(s)	Coordination 5(t)	Coordination 6
	O ₂ N ₄ N ₁ O ₃ O ₁	O ₂ N ₄ N ₁ O ₃ O ₁	
Ni-H ₃ L (101)	280.752	278.322	765.203
(111)	368.651	350.400	915.987
Co-H ₃ L (101)	270.617	285.880	627.189
(111)	281.965	373.855	664.512

(s): square pyramid ; (t): trigonal bipyramid

The results obtained by molecular modelling show that the complexes formed with cobalt(II) are more stable than those of nickel(II) which is in agreement with the stability constants obtained by potentiometry (Table 4).

The optimized geometry for the more stable nickel complexes is square planar and it is an octahedral configuration slightly deformed around the central ion Co(II), where two sites are occupied by two water molecules. [NiHL] and [CoHL(H₂O)₂] structures were depicted in Figs. 5, 6.

Table 4

Steric energies and stability constants of Ni-H₃L and Co-H₃L complexes

Species	Stability constants (log β _{hii})	Steric energies (KJ/mol)
Ni-H ₃ L (101)	7.02	186.882
(111)	12.58	192.560
Co-H ₃ L (101)	9.07	163.308
(111)	15.08	179.240

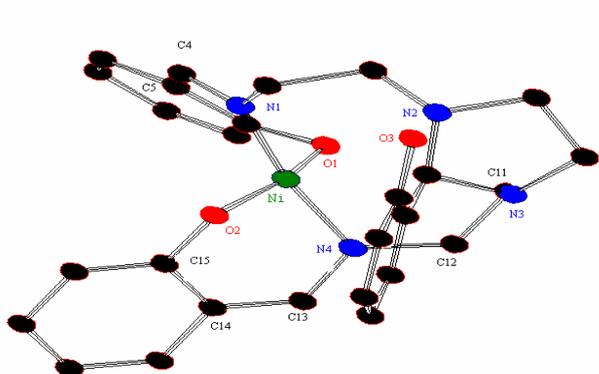
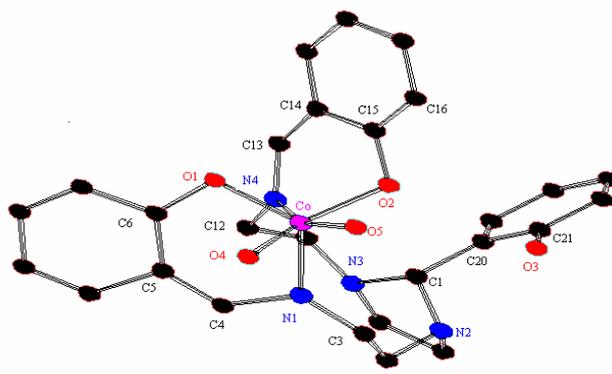


Fig. 5 – [NiHL] complex (coordination 4).

Fig. 6 – [CoHL(H₂O)₂] complex (coordination 6).

EXPERIMENTAL

1. Starting materials

All the chemicals and solvents were of reagent grade materials and were used without further purification. A solution of NaOH (0.1 M, 0.5 M) was prepared from Titrisol Merck. Stock solutions of Co(II) and Ni(II) ions were prepared from chloride Salts (Merck). Doubly distilled water was used for the preparation of solutions. The purity and the concentration of the prepared solution were checked by potentiometric method.

2. Preparation of ligand

The Schiff base (H₃L) has been prepared according to the known procedure¹⁸ with some modification.¹⁹

3. Potentiometric measurements

Potentiometric measurements of the ligand and metal-ligand complexes were carried out using a tacussel pHN-81 pH-meter, which was accurate to 0.01 unit and standardized before each titration using buffer solutions (pH=4.00 and pH=7.00 at 20°C), and a combination electrode placed in a glass vessel (298 K thermostat). The solution of constant ionic strength (I= 0.2 M) was maintained with NaCl (0.5 M). The titration with NaOH (0.1M) was conducted over pH range 2-11. All titration were made in the presence of HCl (Merck) in H₂O (90%) and ethanol (10%) solutions. Atmospheric CO₂ was excluded from the cell during the titration by passing N₂ across the top of the experimental solution in the reaction cell. The concentration of protonated ligand (H₃L) and metal ions in stock solutions used in potentiometric titrations was 10⁻³M.

4. Calculation of equilibrium constants

Protonation constants $K_i^H = \frac{[(H_iL)^{i-3}]/[(H_{i-1}L)^{i-4}][H^+]}{[H^+]}$ were calculated by fitting the potentiometric data obtained for the free ligand using the Irving-Rossotti method²⁰ and Sirko program.¹⁷ Average \bar{n} values were obtained from the titration curves using the following equation was used:

$$\bar{n}_a = y + (V_1 - V_2)(N + E^0) / (V_0 + V_1) T_L^0$$

V₀: volume at the beginning (50ml), N: normality of base (0.1N), T_L⁰: molar concentration of total ligand (10⁻³M), y: the number of protons given (H₃L)

The stability constants $\beta_{nij} = \frac{[M_nH_iL_j]^{2h+i-3j}}{[M^{2+}]^h [H^+]^i [L^{3-}]^j}$ of various species formed in the aqueous solution were calculated from the experimental data corresponding to the titrations which refined using Sirko program. The refinement were repeated until the differences between the calculated and observed pH values for 1:1 system were minimized.

5. Modelling of the Co(II) and Ni(II) chelates

An optimised geometry and minimized steric energy (stretching energy + angle bending energy + rotation energy + Van der Waals energy + electrostatic energy) for all complexes formed in solution were determined by molecular modelling wick carried out by the EMO program^{21,22} using the molecular mechanics (MM2). This program uses the relaxation method (single step method) for the calculations.

CONCLUSIONS

A solution study of the H₃L and its complexes with Ni(II) and Co(II) has been investigated by potentiometry. Five protonation constants have been determined for H₃L by Irving-Rossotti method. The Sirko program confirmed the protonation constants for H₃L and gave the stability constants of its complexes formed at pH= 2.5 to 10. It was found that the stability of Co(II) complexes was markedly higher than those of Ni(II). Distribution species showed that ML⁻ predominate in the basic pH and the MHL complex predominate in the acidic pH.

Molecular modelling showed several possible coordination mode for these metals. The values of steric energy showed that the complexes were more stable when H₃L acts as a tetradentate ligand and Co(II) complexes were more stable than Ni(II) ones. The energies found by EMO are in good agreement with the global formation constants determined by Sirko. The optimized geometry is square-planar for Ni(II) complexes and octahedral for Co(II) ones.

REFERENCES

1. S. Djebbar-Sid, O. Benali-Baitich and J. P. Deloume, *J. Mol. Struct.*, **2001**, 569, 221-128.
2. J. Costamagna, J. Vargas, R. Latorre, A. Alvarado and G. Mena, *Coord. Chem. Rev.*, **1992**, 119, 67-88.
3. S. Belaid, S. Djebbar, O. Benali-Baitich, M. Khan and G. Bouet, *C. R. Chimie*, **2007**, 10, 568-572.
4. S. Belaid, S. Djebbar, O. Benali-Baitich, S. Ghalem, M. Khan and G. Bouet, *Asi. J. Chem.*, **2005**, 17, 811-821.
5. A. Adkhis, S. Djebbar-Sid, O. Benali-Baitich, A. Kadri, M. A. Khan and G. Bouet, *Synth. React. Inorg. Met-Org. Chem.*, **2003**, 33, 35-50.
6. X. Do Thanh, S. Djebbar-Sid, S. Duchene, O. Benali-Baitich, M. A. Khan and G. Bouet, *Biolog. Ryt. Res.*, **2001**, 32, 423-429.
7. X. Do Thanh, S. Djebbar-Sid, O. Benali-Baitich, G. Pehu, M. A. Khan and G. Bouet, *Anticancer Res.*, **2000**, 20, 4639-4642.
8. I. H. Hall C. B. Lackey, T. D. Kistler, R. W. Durham, E. Jouad, M. Khan, X. Do Thanh, S. Djebbar-Sid, O. Benali-Baitich, and G. Bouet, *Die Pharm.*, **2000**, 55, 937-941.
9. H. Hamrit, S. Djebbar-Sid, O. Benali-Baitich, M. A. Khan and G. Bouet, *Synth. React. Inorg. Met-Org. Chem.*, **2000**, 30, 1835-1848.
10. N. Tidjani-Rahmouni, S. Djebbar-Sid, N. Chenah, O. Benali-Baitich, *Synth. React. Inorg. Met Org. Chem.*, **1999**, 29, 979-994.
11. S. Djebbar-Sid, O. Benali-Baitich and J. P. Deloume, *Transit. Metal. Chem.*, **1998**, 23, 443-447.

12. S. Djebbar-Sid, O. Benali-Baitich and J. P. Deloume, *Polyhedron*, **1997**, *16*, 2175-2182.
13. S. Djebbar-Sid, O. Benali-Baitich, M. A. Khan and G. Bouet, *Synth. React. Inorg. Met -Org. Chem.*, **1997**, *27*, 1219-1233.
14. T. Kaliyappan and P. Kannan, *Prog. Polym. Sci.*, **2000**, *25*, 343-370.
15. R. A. Archer, *Coor. Chem. Rev.*, **1993**, *128*, 49-68.
16. R. Ziesel, *Coord. Chem. Rev.*, **1993**, *195*, 216-217.
17. V. I. Vetrogon, N. G. Lukyanenko, M. G. Schwing - Weill and E. Arnaud - Neu, *Talanta*, **1994**, *41*, 2105-2112.
18. T. Isobe, S. Kida and S. Misumi, *Bull. Chem. Soc. Jpn.*, **1967**, *40*, 1862-1863.
19. L. W. Yang, S. Liu, E. Wong, S. J. Retting, and C. Orvig, *Inorg. Chem.*, **1995**, *34*, 2164-2178.
20. H. M. Irving and Rossotti, *J. Amer. Chem. Soc.*, **1954**, 2904-2911.
21. B. Blaive, G. Legsei and R. Lai, *J. Mol. Struc*, **1995**, *345*, 245-250.
22. A. Zinelabedine, A. Bouraoui, M. Fathallah, F. M Henni, B. Blaive and R. Gallo, *J. Mol. Struc.*, **1993**, *286*, 267-274.