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Account / Revue

Complex formation between manganese(II), cobalt(II), nickel(II), copper(II) and a series of new ligands derived from *N*,*N*′-*O*-phenylenebis(salicylideneimine)

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Abstract

A series of new ligands derived from *N*,*N*′-*O*-phenylenebis(salicylideneimine) have been synthesized and characterized by spectrometric methods. Their protonation constants and the stability constants of their complexes with Mn^{2+}, Co^{2+}, Ni^{2+} et Cu^{2+} have been determined by potentiometric methods in a water–ethanol (90:10 v/v) mixture at a 0.2 mol l^{-1} ionic strength (NaCl) and at 25.0 ± 0.1 °C. The Sirko program was used to determine the protonation constants as well as the binding constants of both species $[M(HL)]^+$ and [ML]. The stability order obtained is in agreement with Irving–Williams series. ***To cite this article: S. Belaid et al., C. R. Chimie 10 (2007).***
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Résumé

Une série de nouveaux ligands dérivés de la *N*,*N*′-*O*-phenylenebis(salicylidèneimine)a été synthétisée et caractérisée par les méthodes spectrométriques conventionnelles. L'étude de la complexation des ions métalliques Mn^{2+}, Co^{2+}, Ni^{2+} et Cu^{2+}, par ces ligands, a été effectuée par pH-métrie en milieu eau–éthanol 90 :10 (vol./vol.) à 25 °C ± 0.1 et à force ionique constante 0,2 M en milieu NaCl. Les constantes de protonation des ligands et les constantes de stabilités des deux espèces $[M(HL)]^+$ et [ML] ont été déterminées à l'aide du programme Sirko. L'ordre de stabilité obtenu pour les complexes est en accord avec la série d'Irving et Williams. ***Pour citer cet article : S. Belaid et al., C. R. Chimie 10 (2007).***
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Keywords: Schiff base; Reduction; Potentiometry; Stability constants

Mots-clés : Base de Schiff ; Réduction ; Potentiométrie ; Constantes de stabilités

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1. Introduction

Schiff bases constitute an interesting class of chelating agents. Due to their preparative accessibility, diversity and structure variability, they are capable of coordinating metal ions, giving complexes which exhibit wide applications in biological systems and industrial uses [1–3].

Schiff bases derived from *ortho*-phenylenediamine are of particular interest because of the proximity of the nitrogen atoms, which permits their simultaneous coordination to the same metal cation, leading mainly to stable monomer species [4–6].

However, these Schiff bases can be reduced to the corresponding amine derivatives, which have a higher stability because they are more flexible and not constrained to remaining planar [7–9], and they do not suffer the hydrolytic processes encountered with Schiff base analogues [10].

Our interest in the chemistry of reduced Schiff bases has also stemmed from previous results about antitumor activities of complexes of Cu(II) with a reduced Schiff base [11–13].

In the present work, we report the determination by potentiometric method of the protonation constants of a series of reduced Schiff bases (Fig. 1) derived from *ortho*-phenylenediamine, and stability constants of their complexes with Mn(II), Co(II), Ni(II) and Cu(II) ions.

The aim of this study is the determination of both the effect of the R group and the reduction of the C=N bonds on the stability of the complexes, by comparison of the results with those reported for Schiff base analogues.

2. Experimental

2.1. Reagents

ortho-Phenylenediamine, 3,4-diaminotoluene, 4-chloro-1,2-phenylenediamine and salicylaldehyde were purchased from Fluka and used without further purification.

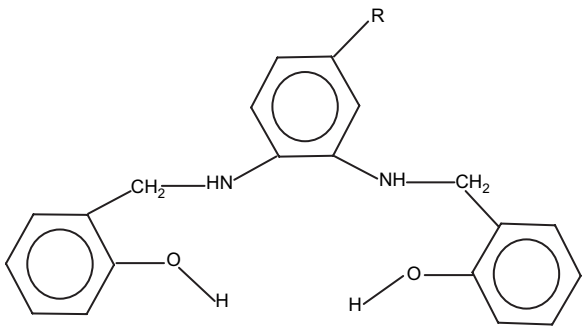

Fig. 1. Formula of ligands: H_2L^1: R = H; H_2L^2: R = CH_3; H_2L^3: R = Cl.

Hexahydrated metal chlorides were obtained from Merck, exact concentrations of metal solutions were determined by titration with EDTA.

Carbonate-free sodium hydroxide used for the potentiometric titrations was prepared and standardized against a standard hydrochloric acid solution.

2.2. Potentiometric measurements

The potentiometric titrations were carried out in water–ethanol (90:10 v/v) solution at a 0.2 mol l^{-1} ionic strength (NaCl) in a thermostated vessel at 25.0 ± 0.1 °C under nitrogen atmosphere. The solutions were titrated with carbonate-free NaOH (0.1 mol l^{-1}), the pH values were measured with a Hanna instruments HI 8417 pH meter.

The pH meter readings in water–ethanol (90:10 v/v) mixture pH(r) differs by an amount from the corrected reading in aqueous medium pH*, according to the equation: $pH^* = pH(r) - \delta$ [14]. The value of δ for water–ethanol (90:10 v/v) mixture was reported to be 0.02. Accordingly, the presence of 10% of ethanol in the solvent has a minor influence on the protonation or the complexes' stability constants obtained.

The measurements were carried out for the ligand alone at the concentration $C_L = 5 \times 10^{-3}$ mol l^{-1}, and for the ligand in the presence of metal cation (ligand/metal ratio 1:1), at the concentration $C_M = C_L = 5 \times 10^{-4}$ mol l^{-1}.

The Sirko program [15] was used to calculate both protonation and stability constants of the ligands and their complexes. Computer-refined values of the constants, corresponding to the minimum standard deviation were retained, and used for the calculation of species distribution.

2.3. Synthesis of ligands

The ligands were synthesized by reduction of Schiff base analogues by $NaBH_4$ [16]. The Schiff bases have been prepared by refluxing in ethanol 2 mmol of salicylaldehyde and 1 mmol of *ortho*-phenylenediamine for H_2L^1, 3,4-diaminotoluene for H_2L^2, 4-chloro-1,2-penylenediamine for H_2L^3. The resulting Schiff bases were recrystallized in ethanol, and then characterized by elemental analysis, NMR and IR.

In order to reduce the imine bonds, 1 mmol of Schiff base was dissolved in absolute ethanol, and 3 mmol of $NaBH_4$ was added in small portions over 1 h. The resulting mixture was stirred for 2 h, during which

time it changed color. Then, the solution was diluted and acidified with hydrochloric acid in order to destroy the excess of $NaBH_4$.

The new ligand was extracted with CH_2Cl_2, the solvent was removed under vacuum and the resulting residue was washed with diethyl ether and stirred in hexane until it was transformed into a solid powder.

The elemental microanalyses were carried out at the Central Service of Analysis, CNRS Vernaison (France). The IR Spectra were recorded on a PerkinElmer spectrum one Fourier transform infrared spectrometer. ^{1}H NMR was recorded on a Jeol Gsx 270 MSB (270 MHz) spectrometer.

3. Results and discussion

3.1. Characterization of ligands

Analytical data: found (calc.) for H_2L^1: C, 75.32 (75.00); H, 6.49 (6.25); N, 8.28 (8.75). For H_2L^2: C, 75.56 (75.44); H, 6.35 (6.58); N, 8.42 (8.38). For H_2L^3: C, 67.56 (67.70); H, 5.49 (5.35); N, 7.45 (7.89); Cl, 10.25 (10.01).

The analysis of IR spectra of the ligands shows the absence of any strong absorption at 1615 cm^{-1} attributable to the imine bond, indicating the reduction of C=N bond to the C–NH one. This is confirmed by the presence of new absorption bands at 3390 cm^{-1} assigned to ν (N–H) of the amino groups [17].

The IR spectra of the ligands exhibit broad medium intensity band in the 3200–3270 cm^{-1} range, which is assigned to the O–H vibrations.

The aromatic rings give an intense band due to C–H deformation at 700 cm^{-1}.

The ^{1}H NMR spectra of the ligands (Table 1) have no azomethine hydrogen peaks at 8.2–8.5 ppm, but show new peaks at 4.2 ppm attributable to the methylene groups. The amine hydrogen peak was not observed.

Nevertheless, these observations support the infrared data, and confirm the reduction of imine bonds to amine ones.

Table 1
^{1}H NMR spectral chemical shifts (δ in ppm)

Ligand	Aromatic protons	CH_2–N	CH_3	–OH
H_2L^1	6.25–6.46 (m) 6.72–7.02 (m) 6.89–7.08 (m)	4.30 (s)		11.25
H_2L^2	6.05–6.18 (m) 6.42–7.05 (m) 6.45–7.02 (m)	4.30 (s)	2.42 (s)	11.08
H_2L^3	6.20–6.48 (m) 6.58–7.12 (m) 6.45–7.06 (m)	4.30 (s)		11.10

Measured as saturated solution in $CDCl_3$, using TMS as the reference, s = singlet, m = multiplet.

Table 2
Protonation constants of the ligands (log K)

Equilibrium	Log K		
	H_2L^1	H_2L^2	H_2L^3
L^{2-}/HL^-	11.30 (±0.04)	12.32 (±0.03)	10.88 (±0.08)
HL^-/H_2L	10.29 (±0.04)	10.76 (±0.02)	9.86 (±0.06)
H_2L/H_3L^+	5.12 (±0.01)	6.02 (±0.04)	4.30 (±0.07)
H_2L/H_3L^+	5.82 (±0.01)	6.75 (±0.04)	4.96 (±0.07)

Water–ethanol (90:10 v/v), $I = 0.2$ M NaCl.

3.2. Potentiometric measurements

The constant β_{pqr} calculated by the Sirko program are defined by the equilibrium:

$$pM^{2+} + qH^+ + rL^{2-} \rightleftarrows [M_pH_qL_r]^{(2p+q-2r)}\beta_{pqr}$$

The successive constants $\log K$ for the ligands calculated from the overall constants $\log \beta_{pqr}$ are listed in Table 2.

The ligands are tetradentate with two adjacent weak amine donors and two strongly basic phenolate groups. Four constants were obtained for each ligand; the basicity sequence obtained is $H_2L^2 > H_2L^1 > H_2L^3$.

The higher basic character of H_2L^2 is attributable to the electron-donor effect of the methyl group; and the lower basic character of H_2L^3 is due to the electron-withdrawing effect of the chloride atom.

Comparison of these results with those reported for Schiff base analogues [4–6] indicates that the protonation constants of these ligands are higher, especially

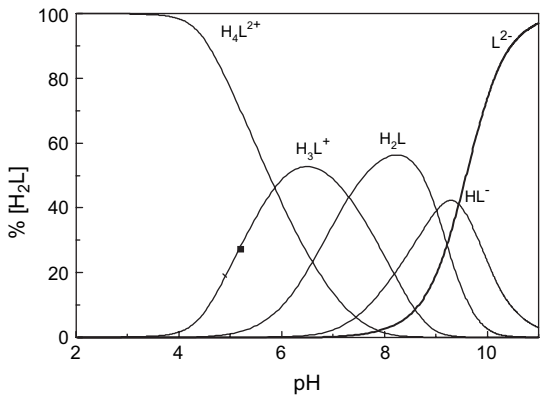

Fig. 2. Species distribution diagram of H_2L^1.

Table 3
Stability constants (log K) for the complexes

Species	Mn	Co	Ni	Cu
$[M(HL^1)]^+$	7.94 (±0.01)	10.32 (±0.10)	10.58 (±0.08)	10.95 (±0.05)
$[ML^1]$	14.23 (±0.04)	16.41 (±0.06)	16.85 (±0.04)	17.31 (±0.01)
$[M(HL^2)]^+$	8.02 (±0.05)	10.87 (±0.04)	11.05 (±0.10)	11.45 (±0.06)
$[ML^2]$	14.81 (±0.06)	17.2 (±0.02)	17.32 (±0.08)	17.81 (±0.04)
$[M(HL^3)]^+$	6.13 (±0.01)	9.81 (±0.07)	9.74 (±0.09)	10.21 (±0.07)
$[ML^3]$	12.48 (±0.07)	15.31 (±0.05)	15.22 (±0.03)	16.1 (±0.08)

Water–ethanol (90:10 v/v), $I = 0.2$ M NaCl.

those assigned to the nitrogen atoms of the amino groups. This arises because the nitrogen atoms of the Schiff base are not able to disperse charge to the solvent by hydrogen bonding [18].

The species distribution diagram as function of pH (Fig. 2) shows that the deprotonation of H_4L^{2+} occur at pH = 4 and leads to the successive formation of H_3L^+, H_2L, HL^- and L^{2-}, the deprotonation of both phenolic groups is completed at pH > 10.

Similar diagrams were obtained for H_2L^2 and H_2L^3.

The stability constants (log K) obtained for the complexes are listed in Table 3. For all the systems studied, only monomer species were formed, the model that best fits the experimental data is the one with formation of two species $[MHL]^+$ and [ML].

The $[MHL]^+$ species may be assumed to be protonated at the phenol oxygen of salicylaldehyde moiety. The complex [ML] results from the coordination of the metal to the ligand fully deprotonated. It is more stable than the complex $[MHL]^+$, indicating that in the ML complex, the ligand is coordinated to the metal by both amino groups and phenolate oxygen atoms.

The systems H_2L^2–M(II) (M(II) = Ni, Cu, Co and Mn) give complexes that are more stable than those for the systems H_2L^1–M(II) due to the electron-donor effect of the methyl group, which is favorable to coordination.

For the systems H_2L^3–M(II), the opposite effect applies and the stability of their complexes are less than those for H_2L^1–M(II) systems, as a consequence of the electron-withdrawing effect of the chloride atom.

Thus, for any metal the stability sequence is $H_2L^2 > H_2L^1 > H_2L^3$ in agreement with the basic character order of these ligands.

For the systems ML ($H_2L = H_2L^1$, H_2L^2, H_2L^3), the stability sequence observed is Cu > Ni > Co > Mn, in agreement with Irving–Williams series.

The complexes of Ni(II) and Co(II) with these ligands are more stable than those reported with Schiff base analogues [4–6]. In fact, the complexes of reduced Schiff bases are expected to be more flexible as they are not constrained to be planar.

The species distribution diagram for Ni–$H_2L^3$and Cu–H_2L^2 systems are reported in Figs. 3 and 4. Similar diagrams were obtained for the other systems.

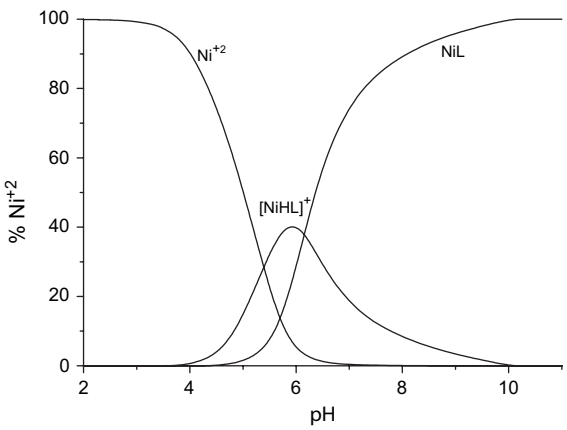

Fig. 3. Species distribution diagram of Ni–H_2L^3.

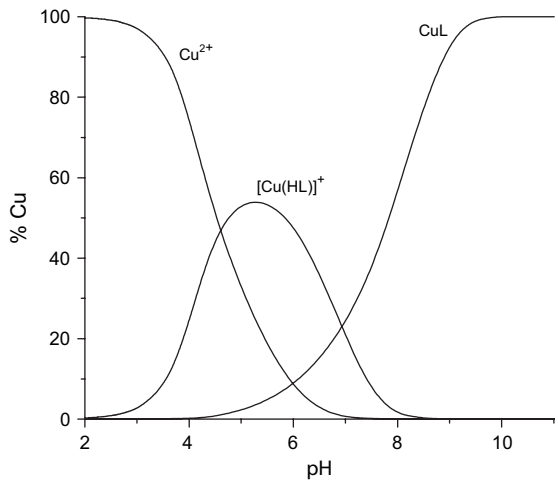

Fig. 4. Species distribution Ni–H_2L^3 diagram of Cu–H_2L^2.

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