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# Study of Co(II) Chlorocomplexes Formation in Methanol and Water Effect on Their Stability

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## Abstract

Formation and stability of Co(II) chlorocomplexes were studied using UV-Vis and near Infra Red spectrophotometry in methanol at 25°C. Formation of three chlorocomplexes and a structural modification  $O_h \rightarrow T_d$  were obtained from the study of the equilibrium:  $Co^{2+} + j Cl^- \rightleftharpoons CoCl_j^{(j-2)-}$ . The stability of the monochlorocomplex was studied by the graphical method of Kruh and the stability constants were calculated with the SIRKO program based on the least-square method, the retained model for the set of all solutions was [1, 2, 3]. Water effect on the stability of the formed complexes was carried out from recorded spectra analysis for different water fractions  $x_{water}$ .

**Key words:** solvent effect, chlorocomplexes, spectrophotometry, stability constant, structural modification.

## 1.Introduction

Complexation plays an important role and gives applications in industrial, pharmaceutical, environmental and energetic domains [1-4]. Formation of octahedral ( $O_h$ ) and tetrahedral ( $T_d$ ) Co(II) complexes is known from solid state studies [5]. The color change of cobalt solutions from pink to blue is known from qualitative studies [6, 7]. Jones [8] and Hantzsch [9] explained this change by the dehydration of solvated Co(II) ion while it is due to complex formation for CrOH [10] and Bassett [11]. Generally, it is well known that hexa aquacobalt(II) ion is converted into Co(II) tétrachloro complex in high chloride concentrated medium [12-17].

Cobalt(II) ; nickel(II) and copper(II) chlorocomplexes have been studied in different solvent namely trimethyl phosphate, acetonitrile (AN), propylene carbonate (PC) and

dimethylformamide (DMF) [18-20] using X-ray diffraction [21], voltametric [22] and calorimetric methods [23].

J. Bjerrum et al. postulated spectrophotometrically the formation of four Co(II) chlorocomplexes in aqueous solution for higher chloride concentrations and calculated their stability constants [24]. However, only one complex of feeble intensity has been reported by Bjerrum [25] and Waki [26].

In 2011, Zhou [27] et al. used the interaction between Co(II) complexes and water to determine its concentration in organic solvents. Silber and Murguia [28] reported the presence of 4 complexes in water and methanol. The recorded spectra in DMF; PC and (DMSO) [29, 30] in the UV-Vis region revealed formation of successive cobalt (II) chlorocomplexes of the general formula:  $[\text{CoCl}_j]^{-(j-2)}$ . The relationship with the dielectric constant of the solvent has been established in DMSO, DMF and PC [31]. In near Infra red region the formation of four Co(II) and Nickel(II) chlorocomplexes has been established in aprotic solvents [30;32]. The stability constant of the formed complexes depends on several factors: electronegativity, nature of the donor atom (hard / soft), structure of the ligand, topology of ligands and the ionic radius, soft or hard metal and its atomic number [33]. However, stability constants of cobalt (II) chlorocomplexes have been calculated in butanol, DMF and AN [34]. Results in the DMSO-ammonium nitrate mixture have also been reported with bromides [35] and chlorides [36]. Hirose [37] gave  $\beta_j$  by combining the spectroscopic and titration methods. In water and in methanol, the presence of two and four species has been respectively reported [28, 38]. In 2-octanol, W. D. BEAVE [39] identified four chlorocomplexes exploring the water effect on their stability.

Mamdouh et al. studied the solvent effect on transition metal complexation and calculated the stability constants [40].

The present paper reports the results of a spectrophotometric study of successive cobalt(II) chloro complexes in the UV-Vis-NIR region; in methanol at 25°C, and investigates the effect of increasing water fractions on the stability of the formed complexes.

## 2. Experimental

Methanol was used without further treatment 99.99%. Stock solutions were prepared from hexahydrate cobalt(II) chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) for the metal ion and from lithium chloride (LiCl) for ligand, subsequent solutions were prepared by dilution.

Mesurments of the absorption variations were performed using an UV-Vis-NIR (200-2000 nm) Jasco V-570 Ubest spectrophotometer at 25°C. The cells length was  $l = 1\text{cm}$  for Vis and NIR and  $l = 2\text{ cm}$  for UV region. An average concentration of  $0.0197\text{ mol L}^{-1}$  for  $\text{Co}^{2+}$  and  $1.89\text{ mol L}^{-1}$  for  $\text{Cl}^-$ , was given by a gravimetric dosage of three solutions.

The final concentration of the metal ion was maintained at  $0.001\text{ mol.L}^{-1}$  for UV measurements;  $2.10^{-2}\text{ mol.L}^{-1}$  for Vis and  $5.10^{-2}$  for NIR. While that of the ligand varied from  $0.01$  to  $1\text{mol.L}^{-1}$  for UV, from  $0.1$  to  $1\text{ mol.L}^{-1}$  for Vis and from  $0.05$  to  $1.8\text{mol.L}^{-1}$  in NIR. Only mononuclear complexes are formed under these experimental conditions and taken into account in the mathematical calculations.

The spectrophotometric reference was a solution of Co(II) in methanol at  $0.001\text{ mol.L}^{-1}$  for UV;  $2.10^{-2}\text{ mol.L}^{-1}$  for Vis and  $5.10^{-2}$  for NIR.

2- In order to follow the water effect on the destruction of the formed complexes, progressive volumes of water ( $V_{\text{water}} = 0,03\text{-}0,5\text{ml}$ ) were added to solutions of different molar ratios (Ligand/Metal) ( $R = 10 ; 15 ; 20 ; 37,5 ; 40 ; 45$  and  $50$ ). The UV-Vis-NIR experimental spectra have been recorded for every molar ratio with different fractions of added water.

### **3 Results and discussion**

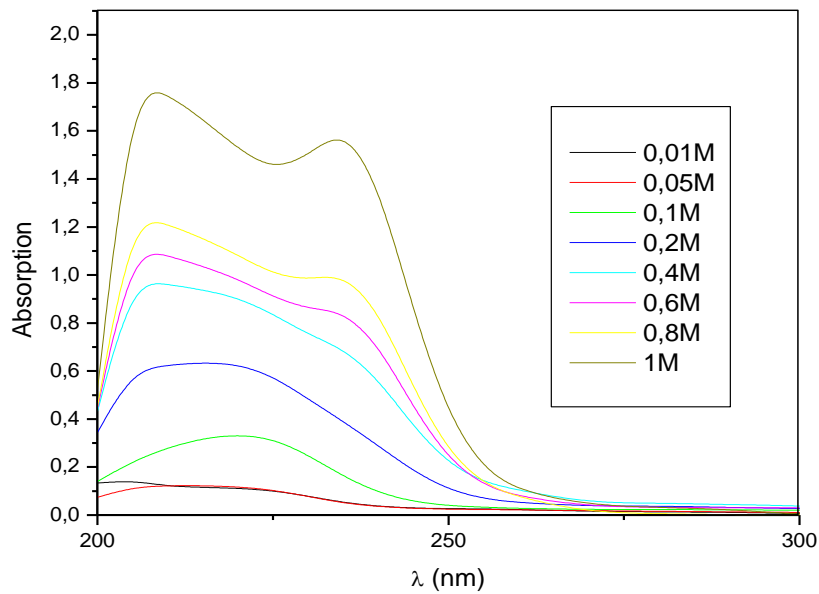
#### **3.1 Experimental spectra:**

A kinetic study performed on the prepared solutions, for the duration of 24 hours, showed that chloride has a lower stability compared to cobalt solutions and ( $\text{Co}^{2+} / \text{Cl}^-$ ) mixtures.

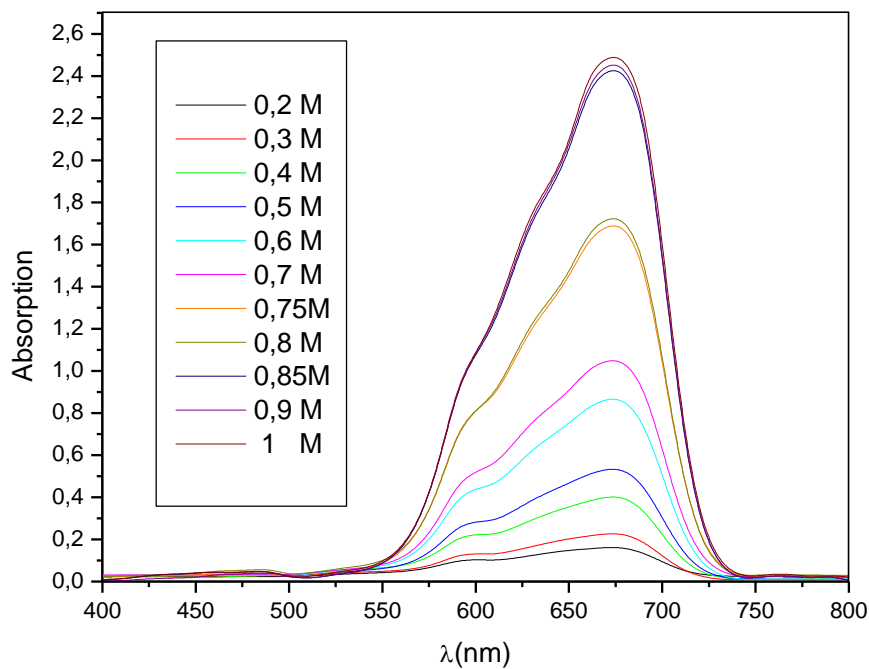
a- UV: solvated  $\text{Co}^{+2}$  ion has a maximum at 205. Addition of  $\text{Cl}^-$  produced a peak at 203 nm which increases significantly by increasing the concentration of  $\text{Cl}^-$  where a bathochromic shift is observed up to 207 nm (Figure 1). A maximum at 220 nm of feeble intensity which shifts to higher wavelengths involving formation of the first chlorocomplex  $\text{CoCl}^+$  [41]. For  $[\text{Cl}^-] = 0,4\text{ mol.L}^{-1}$ , the spectrum exhibits two maxima at 205 nm and 235 nm respectively indicating the formation of a new species. The absorption intensity of these maxima increased for  $[\text{Cl}^-] > 0,4\text{ mol.L}^{-1}$ . If the coordination number of metal ion with coordination 6 and 4 for  $\text{CoCl}^+$  et  $\text{CoCl}_3^-$  respectively, is taken into consideration, the coordination number decreases during the reaction  $\text{CoCl}^+ + 2\text{Cl}^- \rightarrow \text{CoCl}_3^-$  and 4 molecules of solvent simultaneously desolvate the metal ion [42].

b- Vis : solvated  $\text{Co}^{+2}$  ion has a low intensity absorption at 526 nm characteristic of the octahedral structure of  $\text{Co}^{+2}(\text{Co}(\text{solv})_6)^{+2}$  and corresponding to the electronic transition  $[4\text{T}_{1g}(\text{F}) \rightarrow 4\text{T}_{1g}(\text{P})]$  [43]. This peak is accompanied by a large band of feeble intensity between 620 nm and 720 nm. Addition of chloride ions produced a slight bathochromic shift of the uncomplexed  $\text{Co}^{+2}$  band with a slight increase of intensity (Figure 2). These changes indicate the formation of the first chlorocomplex. For  $0,1 \text{ mol.L}^{-1} < [\text{Cl}^-] < 0,6 \text{ mol.L}^{-1}$ , we noted an absorption at 600 nm and a large band at 670 nm which increase in intensity showing the presence of two chlorocomplexes : the mono  $\text{CoCl}^+$  and dichlorocomplexe  $\text{CoCl}_2$ . From a (ligand/metal) ratio = 35, three absorptions bands were clearly distinguished, at 600; 627 and 674 nm. This indicates the formation of  $\text{CoCl}_3^-$  in solution. According to Wendling and Benali- Baitich [44],  $\text{CoCl}_4^{2-}$  is formed but it does not exceed 2.5% even in concentrated solutions.

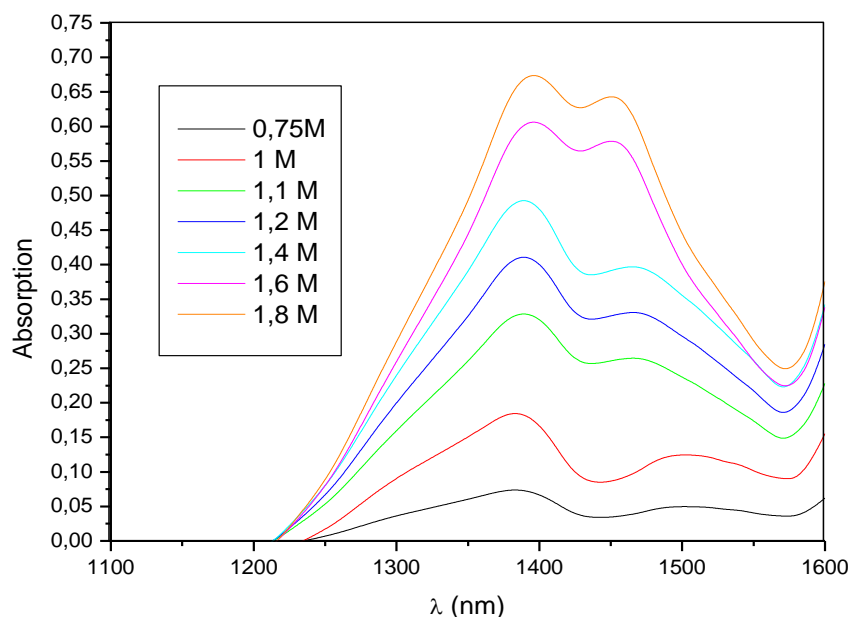
c- Near IR :  $\text{Co}(\text{MeOH})_6^{+2}$  presents a large band of low intensity between 1200 nm and 1400 nm and a max at 1450 nm corresponding to the d-d transition  $[4\text{T}_{1g}(\text{F}) \rightarrow 4\text{T}_{2g}(\text{F})]$ [30]. The recorded spectra of our  $\text{Co}^{+2}$  methanolic solutions exhibited a large band centered at 1300 nm. The first two solutions did not give significant absorptions, due to the presence of  $\text{Co}(\text{II})$  in the reference and the low concentration of  $\text{Cl}^-$  which is unable to form a complex. For chloride concentrations greater than  $0,5 \text{ mol.L}^{-1}$ , we noticed an increase in absorption intensity between 1280 and 1400 nm with a bathochromic shift (Figure 3). The absence of isosbestic points at low  $\text{Cl}^-$  concentrations makes the interpretation about the presence of mono and di chlorocomplexes, more difficult at well-defined concentrations and indicates the instability of  $\text{CoCl}^+$ . The most coordinated species is presented by two separated maxima at 1400 and 1480 nm; according to the results reported in [30]; 3 chlorocomplexes  $\text{CoCl}^+$ ;  $\text{CoCl}_2$  and  $\text{CoCl}_3^-$  are present in solution.



**Figure1** : Absorption Spectra of  $\text{Co}^{+2}\text{-Cl}^-$  methanolic solutions in UV.  $[\text{Co}^{+2}] = 1 \cdot 10^{-3} \text{ mol.L}^{-1}$   $l_{\text{cellule}} = 2 \text{ cm}$ . Ref :  $\text{MeOH} + [\text{Co}^{+2}] = 1 \cdot 10^{-3} \text{ mol.L}^{-1}$ .  $[\text{Cl}^-] = 0,01; 0,05; 0,1; 0,2; 0,4; 0,6; 0,8; \text{ et } 1 \text{ mol.L}^{-1}$



**Figure2** : Absorption Spectra of  $\text{Co}^{+2}\text{-Cl}^-$  methanolic solutions in Vis.  $[\text{Co}^{+2}] = 2 \cdot 10^{-2} \text{ mol.L}^{-1}$ .  $l_{\text{cellule}} = 1 \text{ cm}$ . Ref =  $\text{MeOH} + [\text{Co}^{+2}] = 2 \cdot 10^{-2} \text{ mol.L}^{-1}$ .  $[\text{Cl}^-] = 0,2; 0,3; 0,4; 0,5; 0,6; 0,7; 0,75; 0,8; 0,85; 0,9 \text{ et } 1 \text{ mol.L}^{-1}$ .



**Figure 3:** Absorption Spectra of  $\text{Co}^{+2}\text{-Cl}^-$  methanolic solutions in NIR.  $[\text{Co}^{+2}] = 5.10^{-2} \text{ mol.L}^{-1}$ .  $l_{\text{cellule}} = 1\text{cm}$ . Ref= MeOH+ $[\text{Co}^{+2}] = 5.10^{-2} \text{ mol.L}^{-1}$ .  $[\text{Cl}^-] = 0,75 ; 1 ; 1,1 ; 1,2 ; 1,4 ; 1,6 \text{ et } 1,8 \text{ mol.L}^{-1}$ .

### 3.2. Graphical method of KRUH

In order to calculate the stability constant of the first complex  $\text{CoCl}^+$ , we used the graphical method given by KRUH [45].

$$\frac{b}{A} = \frac{1}{\varepsilon_1 K_1 C} + \frac{1}{\varepsilon_1} \quad (1)$$

b: cobalt concentration,

C: chloride concentration;

A: corrected absorption;

$\varepsilon_1$ : extinction coefficient of the first complex;

$K_1$ : stability constant of the first complex.

The representation of  $b/A$  versus  $1/C$  at given wavelengths, according to (1), gave straight lines where  $\frac{1}{\varepsilon_1}$  and  $\frac{1}{\varepsilon_1 K_1}$  are the intercept and the slope respectively:

In UV,  $K_1$  has been found to be  $4,65 \pm 1,15$  and  $\varepsilon_1 = 1075 \pm 279 \text{ L.mol}^{-1}\text{cm}^{-1}$ .

In the vis region,  $K_1 = 13,49 \pm 8,42$  and  $\varepsilon_1 = 119,8 \pm 27,2 \text{ L.mol}^{-1}\text{cm}^{-1}$ .

Both  $K_1$  and  $\varepsilon_1$  had no significant values in NIR, which confirms the high instability of  $\text{CoCl}^+$  in this region.

### 3.3 Numerical calculation

In order to determine the number of minimum absorbent species present in the solution and calculate their stability constants, spectrophotometric absorption of N solutions at L wavelengths have been treated by the mathematical program SIRKO, details of which are given by Vetrogon et al. [46]. This program uses the matrix rank determination [47] and minimizes the function of the absorption summation by the least-square method:

$$S_l = \sum_{i=1}^N \left[ \frac{d_{i \text{ exp}} - d_{i \text{ cal}}}{d_{i \text{ exp}}} \right]^2 \quad (2)$$

Where  $d_{i \text{ cal}}$  and  $d_{i \text{ exp}}$  are theoretically calculated and experimental absorptions.

The calculation accuracy is judged by the standard deviation  $\sigma$  describing the total arrangement between calculated and experimental data of the whole set of data

$$\langle \sigma \rangle^2 = \frac{\sum_l \sigma_l^2}{L} \quad (3)$$

In the present work, we did not use a supporting electrolyte to maintain the ionic strength ( $\mu$ ) constant. A comparative study had showed that experimental spectra are identical in the presence or in the absence of the supporting electrolyte for weakly concentrated solutions. Concentration of  $\text{Co(II)}$  solutions was  $10^{-2} \text{ mol.L}^{-1}$  which is 200 times less than its solubility in methanol.

For mathematical calculation, several models have been tested in different range of concentration. The best model was retained corresponding to the lower value of  $\sigma$ .

Models have been tested as follows:

UV:

7 solutions solutions : ( N, L ) = ( 7, 9 ) ;  $205 \leq \lambda \leq 245 \text{ nm}$ .

C : 0,05 ; 0,1 ; 0,2 ; 0,4 ; 0,6 ; 0,8 and  $1 \text{ mol.L}^{-1}$ .

5 solutions ( N, L ) = ( 6, 9 ) ;  $205 \leq \lambda \leq 245 \text{ nm}$

[1, 2]: C = 0,01 ; 0,05 ; 0,1 ; 0,2 ; 0,4 and  $0,6 \text{ mol.L}^{-1}$ .

[2, 3] : C = 0,1 ; 0,2 ; 0,4 0,6 ; 0,8 and  $1 \text{ mol.L}^{-1}$ .

[1, 3] : C = 0,05 ; 0,1 ; 0,2 ; 0,4 ; 0,6 and  $0,8 \text{ mol.L}^{-1}$ .



[1, 2, 3] :  $C = 0,05 ; 0,1 ; 0,2 ; 0,4 ; 0,6$  and  $0,8 \text{ mol.L}^{-1}$ .

[1, 2, 3] was retained in the case of 7 solutions, that is the model with the mono-, di- and trichloro complex. Where  $\text{CoCl}_3^-$  showed a lower stability compared to  $\text{CoCl}^+$  and  $\text{CoCl}_2$ . The other models had the lower  $\sigma$  for  $N=6$  and [1, 2] was retained. Results are presented in Table 1.

Vis:

11 solutions (N, L) = ( 11 ,12 ) ;  $550 \leq \lambda \leq 700 \text{ nm}$ .

$C = 0,2 ; 0,3 ; 0,4 ; 0,5 ; 0,6 ; 0,7 ; 0,75 ; 0,8 ; 0,85 ; 0,9$  and  $1 \text{ mol.L}^{-1}$ .

9 solutions: (N, L) = ( 9 ,12 ) ;  $550 \leq \lambda \leq 700 \text{ nm}$ .

[2, 3] :  $C = 0,4 ; 0,5 ; 0,6 ; 0,7 ; 0,75 ; 0,8 ; 0,85 ; 0,9$  and  $1 \text{ mol.L}^{-1}$ .

[1, 2, 3] :  $C = 0,3 ; 0,4 ; 0,5 ; 0,6 ; 0,7 ; 0,75 ; 0,8 ; 0,85$  and  $0,9 \text{ mol.L}^{-1}$

8 solutions: (N, L) = ( 8 ,12 ) ;  $550 \leq \lambda \leq 700 \text{ nm}$ .

[1, 2] :  $C = 0,2 ; 0,3 ; 0,4 ; 0,5 ; 0,6 ; 0,7 ; 0,75$  and  $0,8 \text{ mol.L}^{-1}$ .

[1, 3] :  $C = 0,3 ; 0,4 ; 0,5 ; 0,6 ; 0,7 ; 0,75 ; 0,8$  and  $0,85 \text{ mol.L}^{-1}$ .

For the whole set of 11 solutions the model [1, 2, 3] was favored. Retained results of the other models are presented in Table 2.

NIR : (N, L) = ( 6 , 7 ) ;  $1350 \leq \lambda \leq 1590 \text{ nm}$ .

$C : 1 ; 1,1 ; 1,2 ; 1,4 ; 1,6 ;$  and  $1,8 \text{ mol.L}^{-1}$ .

Both [1, 3] and [1, 3] had no satisfactory results in all tested cases (Table 3), while the model [1, 2, 3] was retained for the whole set of solutions. In this spectral region it is the  $\text{CoCl}^+$  which is unstable compared to  $\text{CoCl}_2$  and  $\text{CoCl}_3^-$ .

**Table 1:** Stability Constants of methanolic cobalt(II) chlorocomplexes in UV :  $205 \leq \lambda \leq 245 \text{ nm}$ ,  
(N, L) = ( 7 , 9 ) for [1, 2, 3], (N, L) = ( 6 , 9 ) for [1, 2] ; [1, 3] and [2 , 3]

Models	[1, 2]	[1, 3]	[2, 3]	[1, 2, 3]
$\beta_1$	$28,96 \pm 15,21$	$31,18 \pm 17,68$	-----	$21,32 \pm 13,48$
$\beta_2$	$37,13 \pm 17,36$	-----	$35,26 \pm 13,63$	$26,47 \pm 14,65$
$\beta_3$	-----	$5,41 \pm 4,76$	$7,81 \pm 4,17$	$3,08 \pm 2,57$
$\langle \sigma \rangle$	0,14	0,25	0,18	0,21

**Table 2:** Stability Constants of methanolic cobalt(II) chlorocomplexes in vis,  $550 \leq \lambda \leq 700$  nm,  $(N, L) = (11, 12)$  for [1, 2, 3];  $(N, L) = (9, 12)$  for [2, 3];  $(N, L) = (8, 12)$  for [1, 2] and [1, 3].

Models	[1, 2]	[1, 3]	[2, 3]	[1, 2, 3]
$\beta_1$	$17,63 \pm 8,41$	-----	-----	$27,83 \pm 11,31$
$\beta_2$	$22,93 \pm 13,79$	-----	$21,92 \pm 14,37$	$42,83 \pm 14,06$
$\beta_3$	-----	-----	$36,81 \pm 11,62$	$38,47 \pm 18,17$
$\langle \sigma \rangle$	0,24	-----	0,19	0,06

**Table 3:** Stability Constants of methanolic cobalt(II) chlorocomplexes in NIR,  $1350 \leq \lambda \leq 1590$  nm,  $(N, L) = (6, 7)$ .

Models	[1, 2]	[1, 3]	[2, 3]	[1, 2, 3]
$\beta_1$	-----	-----	-----	$6,41 \pm 2,93$
$\beta_2$	-----	-----	$23,16 \pm 14,82$	$20,38 \pm 8,53$
$\beta_3$	-----	-----	$9,43 \pm 6,18$	$14,76 \pm 5,72$
$\langle \sigma \rangle$	-----	-----	0,29	0,23

### 3.4. Structural modification

The change of cobalt(II) environment from octahedral of  $O_h$  symmetry to tetrahedral of  $T_d$  symmetry from the addition of first quantities of chloride ion, is shown by the bathochromic shifts noted for Co(II) characteristic bands in recorded experimental spectra and the color change from pale pink in cobalt solution to blue which intensifies with increasing ligand concentration. Reaching a given concentration, the blue color does not undergo any further intensification, indicating that  $T_d$  geometry is reached.

treatment of absorption as a function of ligand concentrations showed that even for higher chloride concentrations and formation of  $CoCl_3^-$ , uncomplexed  $Co^{2+}$  still remains in solution.

### 3.5. Water effect

For fixed concentrations of metal ions ( $[Co^{2+}] = 2.10^{-2} \text{ mol.L}^{-1}$ ), methanolic solutions of different molar ratio were prepared,  $R = 10 ; 15 ; 20 ; 37,5 ; 40 ; 45$  and  $50$  corresponding to

$[Cl^-] = 0,2 ; 0,3 ; 0,4 ; 0,75 ; 0,8 ; 0,9$  and  $1,0 \text{ mol.L}^{-1}$  respectively. For each prepared solution, increasing fractions of water have been added ( $x_{water} = 0,003-0,05$ ). Absorption spectra of all these solutions were recorded in the Vis region.

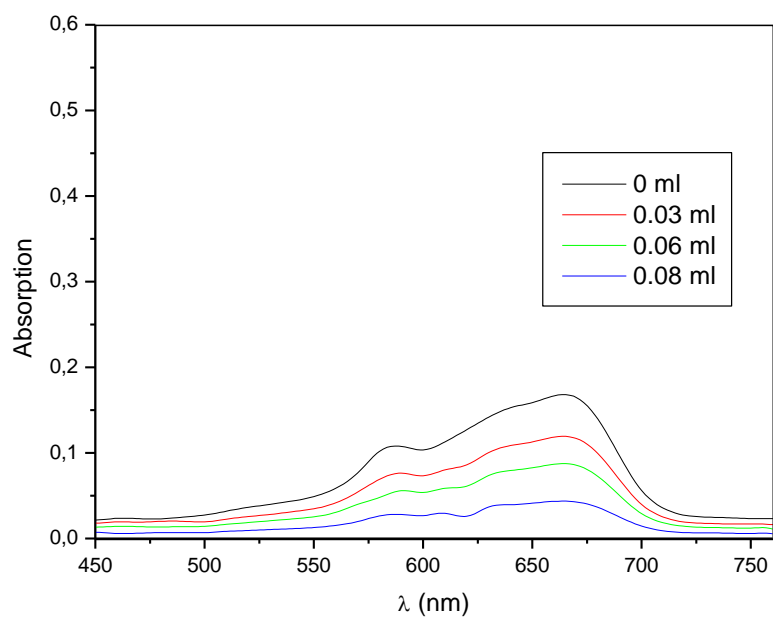
In UV and NIR the same measurements have been carried out with other molar ratios. Recorded spectra showed that water effect is stronger in UV and NIR region, chlorocomplexes are rapidly dissociated and the shape of spectra changes for small water fractions. Results in vis region were suitable to follow progressive changes. Out of these experimental variations of absorption, representative vis spectra of  $R = 10; 37,5$  and  $50$  are respectively presented in figure 4, 5 and 6.

For a solution of  $R = 10$ , the addition of  $x_{water} = 0,003$  keeps the same absorption spectrum and causes a 29% of decrease in the absorption intensity. For  $x_{water} = 0,006$  and  $0,008$ , absorption is reduced to 47.9% and 74% respectively ( $< 0.1$ ) which is out of application of Beer Lambert law. For this molar ratio,  $CoCl^+$  and  $CoCl_2$  are weakly formed and  $x_{water} = 0,006$  is sufficient for their destruction.

The same phenomenon was noted for  $R = 15$  and  $R = 20$ . The characteristic bands lost their absorption intensity and became negligible for  $x_{water} = 0,008$  and  $0,014$  respectively. From calculated percentages of absorption reduction, we can clearly deduce that for fixed chloride concentration, absorption decreases with increasing added water, which confirms that water destroys the formed complexes in methanol. It is well known that the Gutmann donor number of solvents [47] plays a key role in the various complexation reactions [48]. Water exhibits a high solvating ability as its donor number (DN) has a value of 33, and can strongly compete with the ligand molecules. Thus, it is not strange that addition of water to methanol (DN = 19 relatively lower than water); reduces the stability of the formed complexes until their destruction. We may recall here that the high dielectric constant of water ( $\epsilon_{water} = 78,3$ ) for only 33 for methanol, would cause the electrostatic contribution to bond formation to decrease with increasing water quantities in the solvents mixture [50].

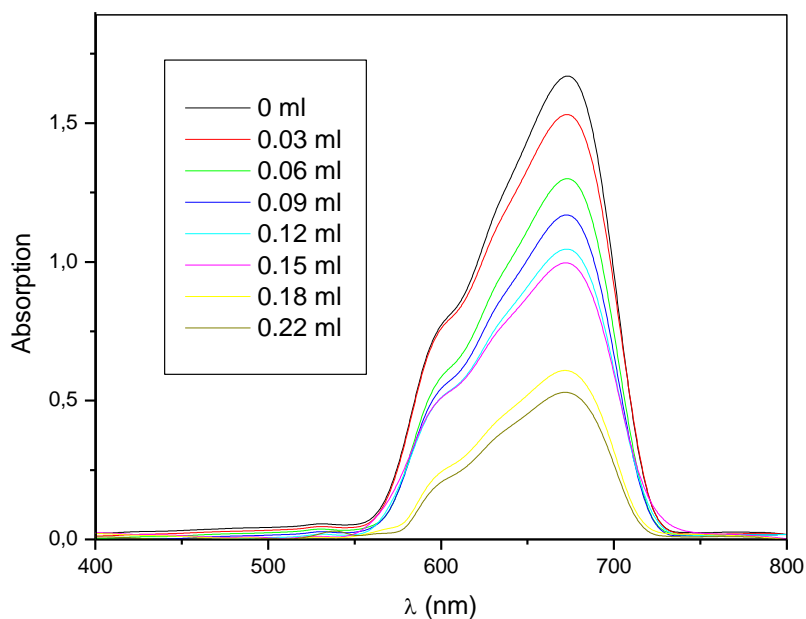
On the other hand, the percentages of absorption reduction vary inversely with chloride concentration. The same fraction of water has a stronger effect on solutions of smaller  $R$ . For a fraction of  $0,003$ , the absorption decrease is 20 times smaller for a solution of double concentration. This is evident since a higher concentration of the ligand, results in a larger amount of  $CoCl^+$  and  $CoCl_2$  formed in solution, subsequently, more co-solvent is needed to

have the same modification as in the less concentrated solutions; fractions of the added co-solvent have been increased for higher molar ratios.



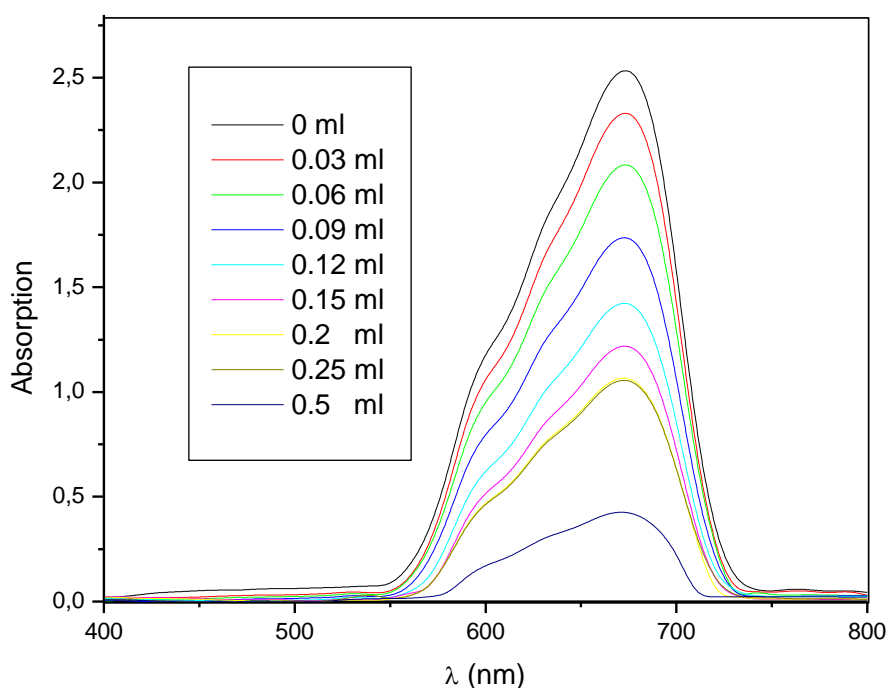
**Figure 4 :** Absorption Vis spectra of  $(\text{Co}^{+2}\text{-Cl}^-)$  solutions in (methanol-water) mixture.  $l= 1 \text{ cm}$ ,  $[\text{Co}^{+2}]= 2.10^{-2} \text{ mol.L}^{-1}$ ,  $[\text{Cl}^-]= 0,2 \text{ mol.L}^{-1}$ , ref: methanol+  $[\text{Co}^{+2}]=2.10^{-2} \text{ mol.L}^{-1}$

For  $R = 37,5$  spectra showed absorptions at 600,630 and 674 nm, three complexes ( $\text{CoCl}^+$ ,  $\text{CoCl}_2$  and  $\text{CoCl}_3^-$ ) are present in solution. The addition of co-solvent produced a decrease of intensity about 72.9% for  $x_{\text{water}} = 0,02$



**Figure 5:** Absorption Vis spectra of  $(\text{Co}^{+2}\text{-Cl}^-)$  solutions in (methanol–water) mixture.  $l=1\text{ cm}$ ,  $[\text{Co}^{+2}]=2.10^{-2}\text{ mol.L}^{-1}$ ,  $[\text{Cl}^-]=0,75\text{ mol.L}^{-1}$ , ref: methanol+  $[\text{Co}^{+2}]=2.10^{-2}\text{ mol.L}^{-1}$ .

For a solution of  $R = 50$ , the addition of water from  $x_{\text{water}} = 0,003$  up to  $x_{\text{water}} = 0,025$  decreased the absorption intensity up to 60%. For  $x_{\text{water}} = 0,05$  the bands shifted slightly and lost their intensity up to 85% forming a large band due to the dissociation of the formed complexes. As previously concluded, we note that even for solutions of high chloride concentration, addition of water causes the dissociation of complexes formed in MeOH depending inversely on the ligand concentration in solution.



**Figure 6:** Absorption Vis spectra of  $(\text{Co}^{+2}\text{-Cl}^-)$  solutions in (methanol–water) mixture.  $l=1\text{ cm}$ ,  $[\text{Co}^{+2}]=2.10^{-2}\text{ mol.L}^{-1}$ ,  $[\text{Cl}^-]=1\text{ mol.L}^{-1}$ , ref: methanol+  $[\text{Co}^{+2}]=2.10^{-2}\text{ mol.L}^{-1}$ .

## Conclusion

The study of formation and stability of Co (II) chlorocomplexes in the UV-Vis-NIR region showed the presence of 3 species in methanol  $\text{CoCl}^+$ ,  $\text{CoCl}_2$  and  $\text{CoCl}_3^-$  with absence of  $\text{CoCl}_4^{2-}$ . Calculated parameters with the program SIRKO showed that  $\text{CoCl}_2$  is more stable than  $\text{CoCl}^+$  et  $\text{CoCl}_3^-$  and for the whole set of solution the model [1, 2, 3] gives the best results. Our results showed an acceptable agreement with those reported in [51], this confirms that the ionic strength has no significant effect on chlorocomplexes stability in diluted solutions. This effect becomes more important by increasing concentration in solution.

The addition of water to (Co<sup>+2</sup>-Cl<sup>-</sup>) solutions dissociates the formed complexes in methanol. Absorption intensity varies inversely with the water fraction at fixed concentration of metal and ligand ions. Spectra have also shown that the same amount of water has a stronger effect on solutions of lower Chloride concentration.

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