



**HAL**  
open science

## Octahedral and tetrahedral con®guration changes of nickel(II) chloro complexes from spectrophotometric studies in aprotic solvents

Abdelghani Chiboub-Fellah, Jean Meullemeestre, Catrin Spies, France Ois Vierling, Mustayeen A Khan

► **To cite this version:**

Abdelghani Chiboub-Fellah, Jean Meullemeestre, Catrin Spies, France Ois Vierling, Mustayeen A Khan. Octahedral and tetrahedral con®guration changes of nickel(II) chloro complexes from spectrophotometric studies in aprotic solvents. *Transition Metal Chemistry*, 1999, 24, pp.135-140. 10.1023/A:1006910310635 . hal-03199274

**HAL Id: hal-03199274**

**<https://univ-angers.hal.science/hal-03199274>**

Submitted on 16 Apr 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinee au depot et  la diffusion de documents scientifiques de niveau recherche, publies ou non, manant des tablissements d'enseignement et de recherche franais ou trangers, des laboratoires publics ou privs.

# Octahedral and tetrahedral configuration changes of nickel(II) chloro complexes from spectrophotometric studies in aprotic solvents

Abdelghani Chiboub-Fellah, Jean Meullemeestre, Catrin Spies and François Vierling\*

Laboratoire de Chimie Physique, C.N.R.S.-U.M.R. 7512, Ecole Européenne de Chimie, Polymères et Matériaux (ECPM), Université Louis Pasteur, 1, rue Blaise-Pascal, 67008 – Strasbourg-Cedex, France

Mustayeen A. Khan

Faculté des Sciences, Université d'Angers, Angers, France

## Summary

Four Ni<sup>II</sup> chloro complexes were identified spectrophotometrically in aprotic media such as DMSO, DMF and propylene carbonate for the first time. An original multiwavelength numerical treatment, based on a Marquardt method, results in the determination of the individual electronic spectra of the mononuclear chloro complexes and of their stability constants, the values of which indicate the presence of rather weak complexes in DMSO and DMF, much stronger in the less solvating propylene carbonate solvent. The overall stability constants calculated for the Ni<sup>II</sup> chloro complexes are:  $\beta_1 = 52$ ,  $\beta_2 = 140$ ,  $\beta_3 = 160$ ,  $\beta_4 = 210$  in DMSO,  $\beta_1 = 60$ ,  $\beta_2 = 110$ ,  $\beta_3 = 900$ ,  $\beta_4 = 15000$  in DMF,  $\beta_1 = 1.6 \times 10^9$ ,  $\beta_2 = 6.4 \times 10^{15}$ ,  $\beta_3 = 2.7 \times 10^{21}$ ,  $\beta_4 = 5.1 \times 10^{26}$  in PC.

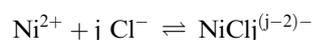
The solvent effect is discussed in terms of the quantitative results obtained from this spectrophotometric study and reveals that the stability of the complexes is an inverse function of the donor properties of the solvent. This result illustrates the general behavior of complex formation in dipolar aprotic solvents, *i.e.* the substitution of one solvent molecule in the inner coordination sphere by the ligand is easier if the solvation strength of the solvent is lower. The solvent effect is also described in terms of the variation of shifts of the calculated absorption maxima for the individual electronic spectra of the chloro complexes. This result is used to identify clearly at which step of coordination the octahedral configuration of the nickel ion changes to the tetrahedral configuration, by comparison with the well-known structural properties of these complexes in the solid state.

## Introduction

We have already reported the results of the behavior of copper(II) chloride complexes in numerous organic solvents<sup>(1–10)</sup>. All the solutions studied were characterized by the presence of four mononuclear copper complexes, the exception being dimethylformamide (DMF) and dimethylsulfoxide (DMSO) where the dichloro complex is absent, probably because of autodecomposition. The apparent stability constants,  $\beta_j$ , of the identified complexes were calculated and, in some cases, interesting relationships between the stability constants

and the molecular weight or the dielectric constant of the solvents were reported<sup>(10,11)</sup>.

In this work we have used the same methodology to investigate the behavior of nickel(II) chloride complexes in different aprotic solvents such as DMF, DMSO and propylene carbonate (PC) with a view to comparing the results with those of copper(II) chloro complexes in the same media. We have, therefore, studied the general equilibria:



and calculated, in the three aprotic solvents, the apparent overall stability constants:

$$\beta_j = [\text{NiCl}_j^{(j-2)-}] / [\text{Ni}^{2+}] \cdot [\text{Cl}^-]^j$$

Nickel(II) chloro complexes have been studied in the solid state and mostly confer a tetrahedral structure upon these complexes<sup>(12–14)</sup>. In aqueous solution, Scarrow and Griffiths<sup>(15)</sup> postulated the presence of the tetrachloronickel complex, however the lack of formation of this compound has been reported by several authors<sup>(16–18)</sup>. For Licheri *et al.* the presence of tri- and tetrachloro complexes in solution seems quite probable<sup>(19)</sup>.

The Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> chloro complexes were studied by Gutmann *et al.* in organic solvents such as trimethylphosphate (TMP), acetonitrile (AN), DMF and PC<sup>(20–22)</sup>. These authors indicated the existence of four mononuclear complexes in each solvent, except in DMF where the dichloro complex autodissociates into mono- and trichloro complexes. However, in none of these studies have the authors reported formation constants. Ishiguro and co-workers have, on the other hand, reported four mononuclear complexes in DMF<sup>(23)</sup>.

We have recently published the results of nickel(II) chloro complexes in alcoholic solutions: methanol (MeOH), ethanol (EtOH) and propanol (*n*-PrOH)<sup>(24)</sup>. In these protic media, at 25 °C and at constant ionic strength (1 mol L<sup>-1</sup>), the formation of only two mononuclear complexes is postulated and their stability constants have been calculated. The present work pertains to the aprotic solvents: DMF, DMSO and PC.

## Experimental

### Reagents

The aprotic solvents were used after several purification steps, in order to eliminate organic compounds or products resulting from possible photochromic degradation. Dehydrated solvents were used and were

\* Author to whom all correspondence should be directed.

considered to be anhydrous if the water content was less than 200 ppm. Dried DMSO (Merck) was purified by two distillations at 45 °C under reduced pressure (1 mm) and over a large CaH<sub>2</sub> surface; less than 100 ppm of H<sub>2</sub>O were found in the purified DMSO. Elleb *et al.*<sup>(1)</sup> showed that small quantities of water do not modify either the stability of the solvent and samples of solutions under study, or their absorption values, within 48 h. However, the solvent was used immediately after purification in order to establish identical experimental conditions for all investigated systems. DMF (Fluka) was distilled under reduced pressure below 80 °C, which corresponds to the onset of decomposition of the solvent. The redistilled DMF contains less than 250 ppm of H<sub>2</sub>O and its purity was checked by conductivity measurements according to the recommendations of Juillard<sup>(25)</sup>. Propylene carbonate (Fluka) was purified in several steps, using the method of Gossé and Denat<sup>(26)</sup>. After 12 h contact with KMnO<sub>4</sub>, the remaining solid was filtered and the dissolved permanganate eliminated by heating for 4 h at 120 °C. After cooling, MnO<sub>2</sub> and the oxidized products (propylene glycol, allyl alcohol and propylene oxide) were separated by filtration. Rapid distillation was performed at 15 mm Hg pressure and the solution was passed through an Al<sub>2</sub>O<sub>3</sub> column in order to remove acidic impurities. The remaining solvent was then redistilled at 68–70 °C (1 mm Hg). The yield is *ca.* 50% and PC has a H<sub>2</sub>O content <100 ppm.

Due to the absorption of both DMSO and DMF the measurements were limited to wavelengths greater than 280 and 260 nm respectively. PC is transparent in the u.v. but limited below 1400 nm in the near i.r., the more specific range d-d transitions in the investigated complexes.

Recrystallized LiCl (Merck) was used for the ligand with LiClO<sub>4</sub> (Fluka) to maintain a constant ionic strength (1 mol L<sup>-1</sup>) in the DMSO and DMF solutions. In PC, due to solubility, the recrystallised Et<sub>4</sub>NCl and Et<sub>4</sub>NClO<sub>4</sub> (Merck) were used in 0.1 mol L<sup>-1</sup> constant ionic strength solutions.

The nickel ion was introduced as Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O. Synthesis of Ni(solvent)<sub>x</sub>(ClO<sub>4</sub>)<sub>2</sub> where x is 4 or 6 is practicable in DMSO and DMF, but dangerous due to possible formation of very unstable alkyl perchlorates. The use of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O instead of anhydrous Ni(ClO<sub>4</sub>)<sub>2</sub> in the solvents under study has no significant effect on the absorption spectra. The metallic ion content is controlled through complexometric titration with EDTA and murexide as indicator at pH 8<sup>(27)</sup>.

#### Measurements

The measurements were performed with a Cary 17D spectrophotometer connected with a Cary Interface to a routine printer (*Star LC-10*) for data collection. The concentrations of the metal ion never exceeded 10<sup>-2</sup> mol L<sup>-1</sup> in order to guarantee accurate absorbance values between 0.2 and 2.0. The spectra were run immediately after mixing the reagents and it took less than 1 min to obtain the absorption curve in the 350 and 750 nm range (or 1000 to 1600 nm in the near i.r.). The solutions were found to be stable for at least 30 min after mixing. Sets of (N,L) significant data points were collected: N and L were the number of solutions and of wavelengths respectively. A set of (N,L) data points

close to (20,40) collected in the visible is sufficient for a reliable numerical analysis and used for the refinement of the constants.

In the DMSO system, (N,L)<sub>vis</sub> = (18,36) and (N,L)<sub>nir</sub> = (10,26); in the DMF system, (N,L)<sub>vis</sub> = (24,47) and (N,L)<sub>nir</sub> = (15,21); in the PC system, (N,L)<sub>vis</sub> = (17,34) and (N,L)<sub>nir</sub> = (17,16).

#### Calculations

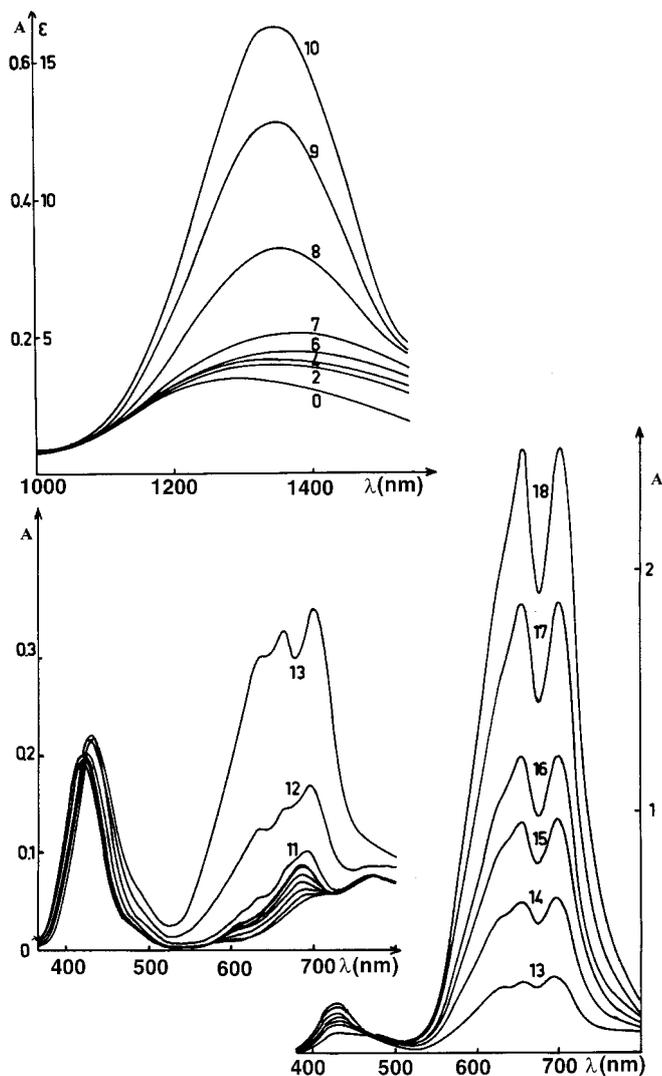
The whole set of spectrophotometric data, (N,L)<sub>vis</sub> + (N,L)<sub>nir</sub>, was analysed using our own multiwavelength program the details of which were given in earlier publications<sup>(1,28)</sup>. For a given model, this program calculates simultaneously two sets of optimized parameters: the overall stability constants ( $\beta_j$ ) and the extinction coefficients ( $\epsilon_j$ ) of all species involved in complexation.

The particular concept used in the algorithm of our program is that the  $\epsilon_j$ s are a function the  $\beta_j$ s in order to minimize the interdependence of these two parameters, which cannot be completely mastered in the optimization process if the  $\epsilon_j$ s and  $\beta_j$ s are defined as identical types of parameters. The quality of the fit is judged for a given model from the value of  $\langle\sigma\rangle$ , the quadratic mean of the standard deviation at each wavelength,  $\sigma_{L,S}$ , obtained in the calculation:  $\langle\sigma\rangle = (\sum\sigma_L^2/L)^{1/2}$ . The deviations of the constants are not always represented in the Tables. These are secondary factors which do not really improve the goodness of the fit. It is necessary, in all programs treating multicomponent systems used hitherto, to postulate supplementary approximations in the vicinity of the minimum of the least squares function and complementary statistical criteria in order to obtain satisfactory values for the deviations of the constants<sup>(28)</sup>.

#### Results and discussion

The spectra of the nickel(II) chloride solutions in DMSO, DMF and PC are shown in Figures 1, 2 and 3 respectively. Regular addition of the chloride ion to the solvated Ni<sup>2+</sup> ion induces a change of the solutions from light green towards blue and indicates the formation of the nickel(II) chloro complexes. The development of the absorption spectra is very similar in all three solvents:

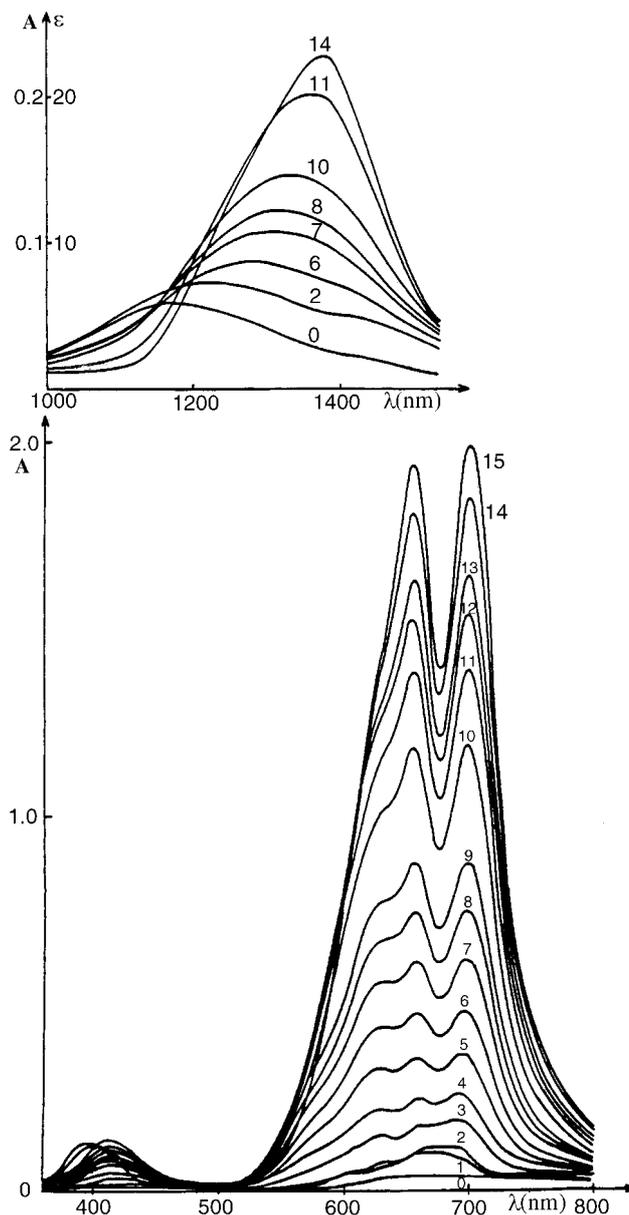
- (i) In the visible range, the nickel(II) absorption in presence of chloride ion is of very weak intensity ( $\epsilon = 20$  l mol<sup>-1</sup> cm<sup>-1</sup>) between 390 and 450 nm, 600 and 750 nm for the lower ligand concentrations. The absorption intensities range between 100 and 300 l mol<sup>-1</sup> cm<sup>-1</sup> and between 600 and 750 nm for higher ligand concentrations;
- (ii) In the near i.r., suitable only in the DMSO and DMF media, the absorption bands, located between 1100 and 1500 nm and corresponding to the <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub> transition, are very broad and of low intensity ( $\epsilon \leq 35$  l mol<sup>-1</sup> cm<sup>-1</sup>);
- (iii) Nickel(II) perchlorate solutions in the three solvents are characteristically octahedral with a typical absorption band of very weak intensity located at *ca.* 400 nm ( $\epsilon \leq 10$  l mol<sup>-1</sup> cm<sup>-1</sup>) with an extended absorption optimally between 660 and 770 nm ( $\epsilon \leq 2$  l mol<sup>-1</sup> cm<sup>-1</sup>) and at 750 nm ( $\epsilon \leq 3.5$  l mol<sup>-1</sup> cm<sup>-1</sup>);
- (iv) The addition of chloride ion, for molecular ratios R < 10, induces a regular shift of the solvated Ni<sup>2+</sup>



**Figure 1.** Absorption spectra of Ni<sup>II</sup>-Li<sup>+</sup>(Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>)-DMSO solutions as a function of lithium chloride analytical concentration (a) vis.: [Ni<sup>2+</sup>]<sub>0</sub> = 5 × 10<sup>-3</sup> mol · L<sup>-1</sup>, [LiCl] range: 0.005–1.0 mol · L<sup>-1</sup>; (l = 4 cm) (b) near i.r.: [Ni<sup>2+</sup>]<sub>0</sub> = 1 × 10<sup>-2</sup> mol · L<sup>-1</sup>, [LiCl] range: 0.01–1.0 mol · L<sup>-1</sup>; (l = 1 cm).

absorption band from 400 to 450 nm with a small intensity. Between 650 and 780 nm the absorption increases leading to an absorption peak at *ca.* 690 nm (Figure 1a). For 10 ≤ R ≤ 20, the absorption band corresponding to the <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(F) transition is characterized by three maxima, at 630, 660 and 695 nm, the intensity of which increase regularly; (v) Finally, at high chloride ion concentrations (20 ≤ R ≤ 100) up to the solubility limit of the chloride ion in the solvents (*ca.* 1 mol L<sup>-1</sup>) the absorption spectra show two important changes: the absorption between 400 and 450 nm diminishes and disappears on one hand whereas on the other the formation of two intense maxima at 655 and 700 nm corresponding to the NiCl<sub>4</sub><sup>2-</sup> ion of tetrahedral symmetry occurs. The stabilisation of these two maxima is already found in PC for R = 5 which is good evidence for a 100% formation of the tetrachloro complex in this solvent.

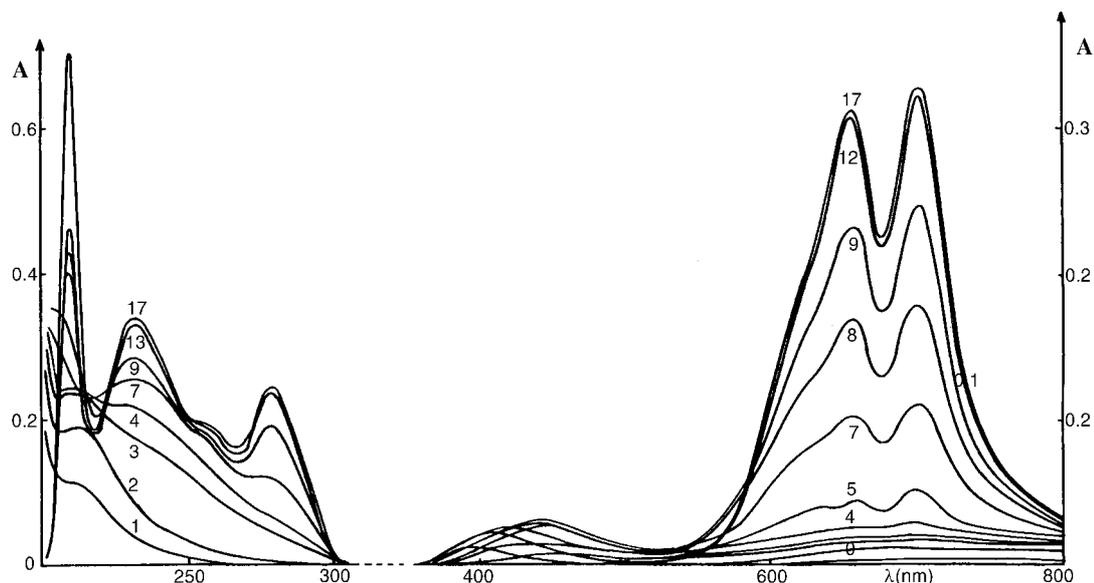
A mathematical treatment of the experimental absorption, A, data was carried out in order to determine the best values of the stability constants. Different theoretical models such as [1,2,4], [1,3,4] and [1,2,3,4] were used, *i.e.* the mono-, di- and tetrachloro complex;



**Figure 2.** Absorption spectra of Ni<sup>II</sup>-Li<sup>+</sup>(Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>)-DMF solutions as a function of lithium chloride analytical concentration (a) vis.: [Ni<sup>2+</sup>]<sub>0</sub> = 1 × 10<sup>-2</sup> mol · L<sup>-1</sup>, [LiCl] range: 0.01–1.0 mol · L<sup>-1</sup>; (l = 1 cm) (b) near i.r.: [Ni<sup>2+</sup>]<sub>0</sub> = 1 × 10<sup>-2</sup> mol · L<sup>-1</sup>, [LiCl] range: 0.01–1.0 mol · L<sup>-1</sup>; (l = 1 cm).

mono-, tri- and tetrachloro complex; mono-, di-, tri- and tetrachloro complex respectively. The model [1,2,3] was not tested as experimental spectra showed definite presence of the tetracoordinated species, the absorption maxima of which are found and calculated in solution and in the solid state<sup>(12,13)</sup>. The detailed results for DMSO are presented in Table 1.

The standard deviations values are highest for the [1,3,4] model, which is therefore rejected. There is not much difference between the values of models [1,2,4] and [1,2,3,4] which is not surprising because autodecomposition of some complexes in aprotic solvents has been reported by Gutmann and has been confirmed in one of our earlier papers<sup>(1)</sup>. However, a closer scrutiny of Table 1 favours the retention of [1,2,3,4] as the best model because all of its standard deviation values, in the visible, in the i.r. and in the total spectral range are lower than those of the [1,2,4] model. Consequently, we



**Figure 3.** UV-visible absorption spectra of  $\text{Ni}^{\text{II}}\text{-Et}_4\text{N}(\text{Cl}^-, \text{ClO}_4^-)\text{-PC}$  solutions as a function of tetraethylammonium chloride analytical concentration  $[\text{Ni}^{2+}]_0 = 4 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{Et}_4\text{NCl}]$  range: 0.0004 – 0.04  $\text{mol} \cdot \text{L}^{-1}$ ; ( $l = 0.2 \text{ cm}$ ).

**Table 1.** Modelling of  $\text{Ni}^{\text{II}}\text{-Li}^+(\text{Cl}^-, \text{ClO}_4^-)\text{-DMSO}$  solutions

| $^a \beta_j (\text{NiCl}_j^{(j-2)-})$    | Model [1,2,4] | [1,3,4]       | [1,2,3,4]     |
|--|---------------|---------------|---------------|
| $\beta_1 (\text{NiCl}^+)$                | $49 \pm 33$   | $42 \pm 25$   | $52 \pm 32$   |
| $\beta_2 (\text{NiCl}_2)$                | $140 \pm 90$  | –             | $140 \pm 60$  |
| $\beta_3 (\text{NiCl}_3^-)$              | –             | $92 \pm 25$   | $160 \pm 80$  |
| $\beta_4 (\text{NiCl}_4^{2-})$           | $310 \pm 250$ | $120 \pm 100$ | $210 \pm 110$ |
| $^b \langle \sigma \rangle_{\text{vis}}$ | 0.081         | 0.099         | 0.080         |
| $\langle \sigma \rangle_{\text{i.r.}}$   | 0.054         | 0.058         | 0.052         |
| $\langle \sigma \rangle_{\text{tot}}$    | 0.071         | 0.084         | 0.069         |

<sup>a</sup> The  $\beta_j'$  values are apparent overall stability constants of the chloro complexes.

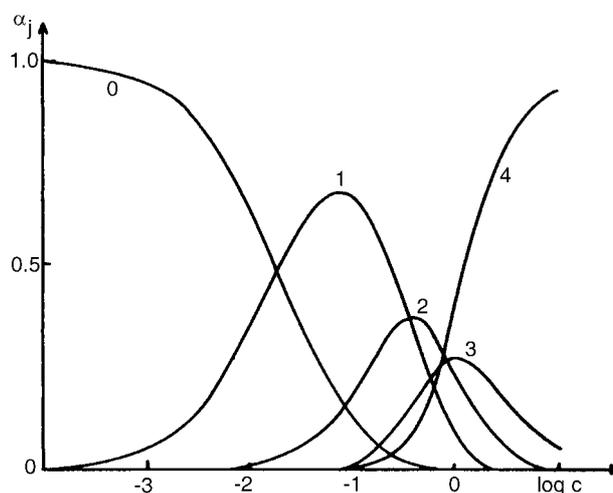
<sup>b</sup>  $\langle \sigma \rangle_{\text{vis}}$  and  $\langle \sigma \rangle_{\text{i.r.}}$  are the standard deviation values for (N,L) sets of data measured for N solutions at L wavelengths in the visible and in the near i.r. respectively.

propose that nickel forms four mononuclear chloro complexes in DMSO for which the stability constants are:  $\beta_1 = 52$ ,  $\beta_2 = 140$ ,  $\beta_3 = 160$  and  $\beta_4 = 210$ .

The formation curves for these complexes are presented in Figure 4 and show the simultaneous existence of at least two absorbing species in any zone of ligand concentration. This fact is the major complication in determining any physical parameters in such systems.

A similar treatment carried out with different models for the data obtained in DMF and PC show that the best model in these solvents is that of four successive mononuclear complexes. The logarithmic values of the overall and the stepwise stability constants, in the three solvents under study, are grouped in Table 2.

The numerical multiwavelength treatment delivers simultaneously with the  $\beta_j$ s values the extinction coefficients  $\epsilon_j$ s of the individual complexes over the whole wavelength range investigated in the visible and near i.r.. These calculated data result in the individual electronic spectra of the complexes, the absorption maxima coordinates of which are summarized in Table 3. Most of the characteristic absorption bands do not undergo any shift as a consequence of the solvent effect. For example, with  $\text{NiCl}^+$ , for all three solvents, the band at  $419 \pm 1 \text{ nm}$  remain unaffected; for  $\text{NiCl}_2$ ,



**Figure 4.** Degree of formation of uncomplexed nickel(II), (curve 0) and of the nickel(II) mono- to tetrachloro complexes (curves 1–4) in DMSO.  $c$  is the free ligand concentration.

the maximum at  $735 \pm 5 \text{ nm}$  and for  $\text{NiCl}_4^{2-}$  three maxima appear unchanged in the three solvents at 620, 655 and 700 nm. However, with  $\text{NiCl}_3^-$ , this is not true and the solvent exercises an important effect creating a significant shift.

It may be recalled that for  $[\text{NiCl}_4]^{2-}$  the tetrahedral structure corresponding to the  $^3T_1(F) \rightarrow ^3T_1(P)$  transition is characterized by maximum absorption bands at *ca.* 1380 nm in the solid state<sup>(12)</sup>. Since we calculated these maxima in solution at 1350 nm in DMSO, and at 1380 nm in DMF, we propose that the structure in solution of this complex is tetrahedral.

According to the absorption maxima coordinates of our calculated individual electronic spectra (Table 3), which are confirmed by the spectroscopic studies in the solid state<sup>(12,13)</sup>, we can deduce the configuration change of the complexes in relation to the coordination step:

(i) For  $[\text{Ni}(\text{sol})_6]^{2+}$ , an octahedral configuration is clearly found in solution and little solvent effect is observed. The small hypsochromic shifts obtained for this

**Table 2.** Logarithm of the apparent overall  $\beta_j$  (stepwise  $K_j$ ) stability constants of Ni<sup>II</sup> chloro complexes calculated for a [1,2,3,4] model in aprotic solvents

| <sup>a</sup> $\epsilon_r$ /DN        | DMSO      | DMF       | PC         |
|--------------------------------------|-----------|-----------|------------|
|                                      | 45/29.8   | 36.1/26.6 | 69/15.1    |
| NiCl <sub>j</sub> (j-2) <sup>-</sup> |           |           |            |
| j = 1                                | 1.7 (1.7) | 1.8 (1.8) | 9.2 (9.2)  |
| j = 2                                | 2.1 (0.4) | 2.1 (0.3) | 15.8 (6.6) |
| j = 3                                | 2.2 (0.1) | 2.9 (0.8) | 21.4 (5.6) |
| j = 4                                | 2.3 (0.1) | 4.1 (1.2) | 26.7 (5.3) |

<sup>a</sup>  $\epsilon_r$  is the value of the dielectric constant in absence of electrolytes. DN is the Gutmann Donor Number.

**Table 3.** Absorption maxima coordinates of the calculated individual spectra of the Ni<sup>II</sup> chloro complexes in aprotic media:  $\lambda_{\max}$ (nm);  $\epsilon_{\max}$ (L mol<sup>-1</sup> cm<sup>-1</sup>)

| Complexes  | DMSO   | DMF  | PC  |
|--|--|--|---|
| Ni(sol <sub>v</sub> ) <sub>6</sub> <sup>2+</sup><br>( <i>O<sub>h</sub></i> ) | 412 (9.6)<br>690 (2.1)sh<br>760 (3.1)sh<br>1300 (3.5)        | 397 (13.8)<br>660 (5.2)sh<br>740 (4.9)sh<br>1190 (6.0)         | 393 (7.8)<br>640 (1.0)sh<br>730 (1.5)sh<br>1170 (4.0)                         |
| NiCl <sup>+</sup>  | –<br>420 (10)<br>690 (5.4)<br>780 (3.8)<br>1350 (5.0)        | –<br>420 (18)<br>685 (10)<br>770 (6.2)sh<br>1300 (7.0)         | <220<br>418 (18)<br>640 (8)sh<br>750 (12)                                     |
| NiCl <sub>2</sub>  | –<br>442 (16.2)<br>730 (<2)                                  | –<br>464 (13.2)<br>730 (25)                                    | 236 (3760)<br>450 (25)<br>740 (4.5)   |
| NiCl <sub>3</sub> <sup>-</sup>   | –<br>–<br>–<br>485 (10)<br>575 (9.2)<br>–<br>–               | –<br>–<br>–<br>580 (178)<br>620 (196)<br>675 (73)<br>1260 (31) | 230 (2560)<br>278 (1660)<br>520 (10)<br>630 sh<br>655 (122)<br>700 (126)<br>– |
| NiCl <sub>4</sub> <sup>2-</sup><br>( <i>T<sub>d</sub></i> )                  | –<br>–<br>–<br>620 sh<br>655 (310)<br>700 (320)<br>1350 (40) | –<br>–<br>–<br>620 sh<br>655 (212)<br>700 (216)<br>1380 (24)   | 232 (4160)<br>255 sh<br>279 (2950)<br>620 sh<br>655 (192)<br>701 (200)<br>–   |

octahedral complex, on going from DMSO to PC, induces the following spectrochemical sequence for the crystal field parameter:  $Dq(\text{DMSO}) < Dq(\text{DMF}) < Dq(\text{PC})$ . This sequence is inverse of the donor numbers of the solvents;

(ii) in the same way, the calculated absorption coordinates for the [NiCl<sub>4</sub>]<sup>2-</sup> spectrum in all three solvents are identical to these observed in the solid state and confirm the tetrahedral configuration for the tetracoordinated nickel(II) complex.

The octahedral-tetrahedral change in the successive nickel(II) chloro complexes can be postulated on the basis of different absorption maxima shifts. The octahedral configuration is not modified for [Ni(sol<sub>v</sub>)<sub>6</sub>]<sup>2+</sup> and [NiCl]<sup>+</sup>. For NiCl<sub>2</sub>, the calculated absorption maxima are clearly different to those of the solvated nickel(II) ion and of the monochloro complex; either bathochromic or hypsochromic shifts are observed in the three solvents. These results are related to the fact that the octahedral configuration of the nickel is significantly changed as a second solvent molecule is

substituted by the chloride ion in the inner coordination sphere. Consequently, we postulate that the breaking of the octahedral configuration {*O<sub>h</sub>* symmetry for [Ni(sol<sub>v</sub>)<sub>6</sub>]<sup>2+</sup>} towards the tetrahedral configuration {*T<sub>d</sub>* symmetry for [NiCl<sub>4</sub>]<sup>2-</sup>} occurs with the NiCl<sub>2</sub> coordination step.

Eventually, it is the stability of the complexes which is the most interesting parameter under study. Table 2 shows that stability increases as an inverse function of the donor number of the solvent. It can also be said that stability is nearly the same in case of DMSO and DMF which have comparable values of the donor number of the solvents whereas in the case of PC, which has a low donor number value, the stability increases sharply. This steep increase of stability in PC has been underlined for copper(II) chloro complexes by Scharff<sup>(29)</sup> and Elleb<sup>(2)</sup> and is probably due to its low donor number value or in other context its low value of the ratio of its molecular weight and the dielectric constant. This ratio is only  $102/69 = 1.48$  and is much higher for the other two solvents.

The lower values of the stability constants in DMF and DMSO indicate the formation of weak complexes whereas stronger complexes are formed in the case of PC. A comparison of  $\log \beta_1$  values of the nickel(II) and copper(II) chloro complexes in the three solvents is given in Table 4.

It is seen that the stability constants evolve in a similar manner for the two metals. We have recently shown that the complexes of cobalt, nickel and copper in alcohols, *i.e.*, the protic solvents, have increasing stability with respect to the atomic number of the metal<sup>(30)</sup>. This is in accordance with the Irving-Williams order of stabilities.

## Conclusions

The octahedral-tetrahedral configuration changes of the nickel(II) chloro complexes has been carefully confirmed according to the solid state results. These results were ascertained from the multiwavelength numerical interpretation of the absorption data measured over the UV, visible and near i.r. in the aprotic DMSO, DMF and PC solutions.

Four mononuclear chloro complexes of nickel(II) are clearly identified and characterized by the apparent stability constants and their individual electronic spectra. The stability order of these complexes is in excellent accord with the inverse order of the donor number of the solvents. This was postulated qualitatively earlier<sup>(20–22)</sup> and is demonstrated now by the numerical interpretation of the spectra measured in the u.v. visible and near i.r. regions. The conclusions reliably set, for the first time on an original quantitative analysis<sup>(28)</sup>, proposed here and not very often performed elsewhere, improve the thermodynamic model of the ability of

**Table 4.** Comparison of  $\log \beta_1$  values of the Ni<sup>II</sup> and Cu<sup>II</sup> chloro complexes in DMSO, DMF and PC

| Solvent | Nickel(II) | Copper(II) |
|---------|------------|------------|
| DMSO    | 1.7        | 3.8        |
| DMF     | 1.8        | 3.0        |
| PC      | 9.2        | 12.0       |

**Table 5.** Spectroscopic shifts [ $\text{cm}^{-1}$ ] of the principal absorption band of the  $\text{NiCl}_j^{(j-2)-}$  complexes,  $\lambda_{\text{max}}[\text{nm}]$ 

| $\text{NiCl}_j^{(j-2)-}$       | DMSO | DMF  | PC   | $^a \delta_s [\text{cm}^{-1}]$ |
|--------------------------------|------|------|------|--------------------------------|
| $j = 1$                        | 420  | 420  | 418  | 100                            |
| $j = 2$                        | 442  | 464  | 450  | 1100                           |
| $j = 3$                        | 575  | 620  | 655  | 2100                           |
| $j = 4$                        | 700  | 700  | 701  | 0                              |
| $^a \delta_n [\text{cm}^{-1}]$ | 9500 | 9500 | 9600 |                                |

$^a \delta_s$ : bathochromic shift as a function of  $n$ , number of coordinated ligands,  $\delta_n$ : spectroscopic shift as a function of the donor power of the solvent.

substitution of the solvent molecules in the inner coordination sphere of the metal ion.

The calculated electronic spectra of the nickel(II) chloro complexes induces some conclusions regarding the solvent effect: for example the study of the bathochromic shift of the absorption maxima of the most important band of the the different  $\text{NiCl}_j^{(j-2)-}$  complexes, reported in Table 5. In this Table,  $\delta_n$  is the spectroscopic shift as a function of  $n$ , the number of chloride ions bound to the metal ion;  $\delta_s$  is the spectroscopic shift as a function of the decreasing donor power of the solvent:

- (i) For each solvent,  $\delta_n$  has practically a constant value of  $9500 \text{ cm}^{-1}$ ;
- (ii) Considering the complex of the same rank,  $\delta_s$  changes irregularly with the donor power of the solvent; the most important intensity of  $\delta_s$  is  $2100 \text{ cm}^{-1}$ ;
- (iii) For the  $[\text{NiCl}_4]^{2-}$  complex,  $\delta_s$  is zero which is in good agreement with the fact that the tetrachloro complex is unsolvated in all solvents investigated.

For the complexed nickel ion, the modification of the octahedral configuration occurs essentially between the formation of  $\text{NiCl}_2$  and  $[\text{NiCl}_3]^-$  species; the very high value of  $\delta_n$   $9500 \text{ cm}^{-1}$  illustrates the difference of configuration of the nickel(II) ion between  $[\text{NiCl}]^+$ ,  $\text{NiCl}_2$  (octahedral) and  $[\text{NiCl}_3]^-$ ,  $[\text{NiCl}_4]^{2-}$  (tetrahedral).

A further study of cobalt(II) chloro complexes in these aprotic media will confirm if this order of stabilities is valid for this system in aprotic medium and improve the conclusions obtained from the evolution of the spectroscopic shifts of the absorption maxima of these mononuclear chloro complexes.

## References

- (1) M. Elleb, J. Meullemeestre, M. J. Schwing and F. Vierling, *Inorg. Chem.*, **19**, 2699 (1980).
- (2) M. Elleb, J. Meullemeestre, M. J. Schwing and F. Vierling, *Inorg. Chem.*, **21**, 1477 (1982).
- (3) M. A. Khan, J. Meullemeestre, M. J. Schwing and F. Vierling, *Polyhedron*, **2**, 459 (1983).
- (4) C. Amuli, J. Meullemeestre, M. J. Schwing and F. Vierling, *Inorg. Chem.*, **22**, 3567 (1983).
- (5) C. Amuli, J. Meullemeestre, M. J. Schwing and F. Vierling, *Inorg. Chem.*, **25**, 856 (1986).
- (6) C. Amuli, J. Meullemeestre, M. J. Schwing and F. Vierling, *Nouv. J. Chim.*, **11**, 27 (1987).
- (7) M. A. Khan, J. Meullemeestre, M. J. Schwing and F. Vierling, *Inorg. Chem.*, **28**, 3306 (1989).
- (8) S. Chafaa, T. Douadi, M. A. Khan, J. Meullemeestre, M. J. Schwing and F. Vierling *Nouv. J. Chim.*, **15**, 39 (1991).
- (9) S. Dali, F. Benghanem, M. A. Khan, J. Meullemeestre, M. J. Schwing and F. Vierling, *Polyhedron*, **10**, 2529 (1991).
- (10) E. Bentouhami, M. A. Khan, J. Meullemeestre, M. J. Schwing and F. Vierling, *Polyhedron*, **11**, 2179 (1992).
- (11) F. Djabi, J. Meullemeestre, F. Vierling, G. Bouet and M. A. Khan, *Bull. Soc. Chim. Fr.*, **131**, 53 (1994).
- (12) F. A. Cotton, R. Francis, *J. Am. Chem. Soc.*, **82**, 2896 (1960).
- (13) F. A. Cotton, O. D. Faut, D. M. L. Goodgame, *J. Am. Chem. Soc.*, **83**, 344 (1961).
- (14) D. M. L. Goodgame, M. Goodgame, F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).
- (15) R. K. Scarrow, T. R. Griffiths, *Chem. Comm.*, 425 (1967).
- (16) N. S. Gill, R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).
- (17) A. B. Blake, F. A. Cotton, *Inorg. Chem.*, **1**, 5 (1964).
- (18) E. Wendling, O. Benali-Ba, G. Yaker, *Revue Chim. Min.*, **8**, 559 (1971).
- (19) G. Licheri, G. Paschina, G. Piccaluga, G. Pinna, *J. Chem. Phys.*, **79**, 2168 (1983).
- (20) V. Gutmann, G. Hampel, R. G. Masaguer, *Monatsh. Chem.*, **94**, 822 (1963).
- (21) H. Hubacek, B. Stancie, V. Gutmann, *Monatsh. Chem.*, **94**, 1118 (1963).
- (22) V. Gutmann, H. Bardy, *Monatsh. Chem.*, **99**, 763 (1968).
- (23) S. Ishiguro, K. Ozutsumil, H. Ohtaki, *Bull. Soc. Chim. Japan*, **60**, 531 (1987).
- (24) M. A. Khan, D. Cronier, G. Bouet and F. Vierling, *Transition Met. Chem.*, **20**, 369 (1995).
- (25) J. Juillard, *Pure Appl. Chem.*, **49**, 885 (1977).
- (26) B. Gossè, A. Denat, *J. Electroanal. Chem. Interfacial Electrochem.*, **56**, 129 (1974).
- (27) H. A. Flaschka, *EDTA Titrations*, Pergamon Press, 1964 p 80.
- (28) F. Vierling, M. J. Schwing, J. Meullemeestre, "Spectra 2000", **79**, 25 (1982).
- (29) J. P. Scharff, *Bull. Soc. Chim. Fr.*, **1**, 413 (1972).
- (30) M. A. Khan, G. Bouet, F. Vierling, J. Meullemeestre and M. J. Schwing *Transition Met. Chem.*, **21**, 231 (1996).

(Received 14 May 1998;

Accepted 02 July 1998)

TMC 4252