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Dicyanamide ions as complexing agents of Co(II): From weak ligands in water to strong ones in an ionic liquid.

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ABSTRACT

The complexation of cobalt cations (Co(II)) by dicyanamide (DCA⁻) in water and 1-butyl-1-methylpyrrolidiniumbis(trifluoromethanesulfonyl)imide ([C₁C₄Pyrr][NTf₂]) has been investigated by recording UV-vis spectra at 20 °C for solutions containing different ratios for the concentrations of DCA⁻ vs. Co(II) ($R = [\text{DCA}^-]/[\text{Co(II)}]$). The variation of the absorbance at a fixed wavelength as a function of R was expressed using the Beer Lambert law, based on a chemical model assuming the formation of up to four successive cobalt-dicyanamide complexes. This allowed us to determine the speciation of cobalt and the complexation constants of all complexes in both aqueous and ionic liquid media. In water, a unique complex of $[\text{Co}(\text{H}_2\text{O})_5(\text{DCA})]^+$ exhibiting a weak complexation constant ($K = 20.5$) is observed. In the ionic liquid, cobalt is shown to coordinate with up to four dicyanamide anions. All species coexist until the ratio R reaches 5000 where more than 90 % of the fourth and last complex $[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})_4]^{(x-5)}$ is formed. In addition, the extraction of cobalt towards hydrophobic ionic liquids trihexyltetradecylphosphonium dicyanamide ([P₆₆₆₁₄][DCA]) and trihexyltetradecylphosphonium bis(trifluoromethanesulfonyl)imide ([P₆₆₆₁₄][NTf₂]) was carried out using various concentration of DCA both in the aqueous and ionic liquid phases. Results were found to correlate very well with the speciation of Co(II) obtained in this work.

KEY WORDS

- Cobalt complexes
- Dicyanamide ions
- Ionic liquids

- Ad hoc modelling
- Metal extraction

1) INTRODUCTION

Cobalt is a light metal located on column 9 of the first period of the transition elements in Mendeleïev's table. Because of its magnetic and physical properties, cobalt is used in numerous applications ranging from anti-corrosion alloys^[1,2], catalysis,^[3-6] permanent magnets^[7-10] and electrode materials for rechargeable batteries.^[11-14] Because the production of energy storage devices is strongly increasing with the development of renewable energy sources, portable communication systems and battery-driven electric vehicles, now-a-days cobalt has become a key metal in high-end devices.

With the development of a sustainable chemistry based on the green chemistry principles as proposed by Anastas,^[15] a major effort is currently undergone in order to set up chemical processes not using hazardous substances and not generating polluting effluents. Volatile organic solvents that are currently widely used in such processes can be replaced by safe, non-flammable and non-volatile ionic liquids (ILs). ILs are composed only of cations and anions and are generally defined as salts melting below 100°C.^[16] Among them, ILs exhibiting melting points below 25°C, called room temperature ionic liquids (RTILs), are of particular interest and the subject of intense research.^[17-19] Because their physical properties can be tuned by simply undertaking structural modifications, RTILs are an attractive class of ILs to be used as a replacement for traditional organic solvents. All the ionic liquids used in this paper are RTILs.

Our team is focusing on the recycling of metals using liquid-liquid extraction which is a very popular and efficient process for ion recovery. By definition, liquid-liquid extraction must be performed between two immiscible phases, usually an aqueous one containing the metal ion and an organic phase where the complexation and extraction of the ion occur. Fluorinated ILs based on NTf₂⁻ (bis(trifluoromethanesulfonyl)imide) are widely used because they yield extracting

phases with an increased hydrophobicity and a low viscosity.^[20,21] Ionic liquids containing a cyclic quaternary ammonium and two alkyl chains, such as 1-butyl-1-methylpyrrolidinium hereafter noted as $[C_1C_4Pyr]^+$, also show a low viscosity which makes them easy to handle.^[19] 1-butyl-1-methylpyrrolidiniumbis(trifluoromethanesulfonyl)imide ionic liquid is thus a prominent candidate for liquid-liquid extraction because of its low viscosity, hydrophobicity and ability to form ion pairs, yielding an efficient extraction of metals from an aqueous phase. Recent reports have showed that several metals, such as Co, Cu or Pd, could be extracted towards ionic liquids in the form of negatively charged complexes composed with anions from the IL, namely Cl^- or Br^- .^[22–24] Several studies have reported the speciation of cobalt in aqueous phases containing chloride,^[25,26] bromide^[26] or dicyanamide^[27] anions. With chloride anions for instance, cobalt(II) is able to form a tetrachlorocobaltate(II) complex when the concentration of Cl^- in the aqueous phase is high, typically above 8 mol.L^{-1} . When dicyanamide ions are present in water, V.H. Köhler et al. showed cobalt was only able to coordinate with one such anion.^[27]

In ionic liquids, reports dealing with the speciation of such light metals are extremely scarce. Some reports have investigated the speciation of chlorometallates^[28,29] or cobalt complexes^[30] in ionic liquids and its interest in the extraction of these complexes towards an ionic liquid was discussed. In addition, some evidence for the complexation of Co(II) with three bis(trifluoromethanesulfonyl)imide anions in neat 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide was also recently given.^[31]

DCA^- is an anion exhibiting a significant delocalisation of charge and a light molecular weight. Many ILs based on this anion were found to be liquid at room temperature, to exhibit very low viscosities as well as toxicities significantly lower than those of the NTf_2 -based ILs.^[19,32] Most DCA -based ILs are however soluble in water and are thus not adapted to the extraction of metal

ions from an aqueous phase. One solution would then be to dissolve such an ionic liquid in a hydrophobic one based on NTf_2^- anion for instance. Another solution, reported in a few articles, is to combine DCA with a large cation, yielding hydrophobic ionic liquids that were then successfully applied to the liquid-liquid extraction of various metal ions.^[33,34] In such studies, the ionic liquid phases were found to exhibit colours not corresponding to the classical chlorometallate or NTf_2^- -metallate complexes. This indicated that DCA^- was complexing with the metal ions and that it was a good ligand for extracting metals into an ionic liquid.

So far, however, neither specific details on the speciation of Co(II) in an ionic liquid containing a dicyanamide anion, nor on the competition between two anions, such as $[\text{NTf}_2]^-$ and DCA^- from an ionic liquid mixture for the Co(II) coordination sphere are reported. In order to gain insights into the extraction mechanisms of such metal ions extracted towards an ionic liquid phase containing DCA anions, knowledge on the exact speciation of a metal within both the aqueous and ionic liquid phases is crucial. $[\text{P}_{66614}]^+$ cation was initially chosen because it forms hydrophobic ionic liquids when combined with $[\text{DCA}]^-$ anions. However, the presence of impurities in phosphonium ILs, hindered using them for spectrometric analysis. $[\text{C}_1\text{C}_4\text{Pyrr}][\text{NTf}_2]$ was then chosen because it presents a high purity. Furthermore, this cation was used by Bortolini et al. to study the speciation of Co(II) in an $[\text{NTf}_2]$ based ionic liquid. The focus of this work is thus to study the speciation of Co(II) in the presence of dicyanamide, in an aqueous phase or in $[\text{C}_1\text{C}_4\text{Pyrr}][\text{NTf}_2]$. In order to reduce the number of ions in the IL phase and to ensure a good solubility of the dicyanamide salt in $[\text{C}_1\text{C}_4\text{Pyrr}][\text{NTf}_2]$, $[\text{C}_1\text{C}_4\text{Pyrr}][\text{DCA}]$ was used as a source of DCA^- anion.

In this article, the molar extinction coefficient of Co(II) dissolved in either solvents, as a function of increasing amounts of $[\text{DCA}^-]$ will be first presented. The concentration ratio $R = [\text{DCA}^-]$

$]/[\text{Co(II)}]$ ranges from respectively 0 to 200 and 0 to 5040 in the aqueous and ionic liquid system. Then, a general model for the speciation of Co(II) will be developed in order to describe the experimental spectra recorded. The speciation of Co(II) in both phases, as calculated within the model will be detailed and discussed.

Finally, in order to illustrate the interest of our results to the field of liquid-liquid extraction, cobalt(II) will be extracted from an aqueous phase using various $[\text{DCA}]/[\text{Co}]$ ratios towards a mixture of ionic liquids containing various $[\text{DCA}]/[\text{NTf}_2]$ ratios.

2) EXPERIMENTAL SECTION

2.1 Chemicals

The ionic liquids, 1-butyl-1-methylpyrrolidinium dicyanamide, $[\text{C}_1\text{C}_4\text{Pyrr}][\text{DCA}]$ (purity 99.5 %) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide $[\text{C}_1\text{C}_4\text{Pyrr}][\text{NTf}_2]$ (purity 99.5 %) were purchased from Solvionic and used after being dried for 12 hours under vacuum. Sodium dicyanamide, $\text{NaN}(\text{CN})_2$ (purity 96 %) so called Na(DCA) was provided by Alfa Aesar. Cobalt(II) sulfate, $\text{Co}(\text{SO}_4)$ (purity > 99 %) was obtained from Acros Organics. Cobalt(II) bis(trifluoromethylsulfonyl)imide, $\text{Co}(\text{NTf}_2)_2$ (purity 99.5 %) was purchased from Solvionic. Water was always taken from MQ-grade water (18.2 M Ω .cm electrical resistivity at 25°C). Trihexyltetradecylphosphonium dicyanamide $[\text{P}_{66614}][\text{DCA}]$ and trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide $[\text{P}_{66614}][\text{NTf}_2]$ (purity 97.0 %) were purchased from Cytec (Solvay) and were used without any purifications.

2.2 Sample preparation

In order to study cobalt dicyanamide complexes in water, two stock solutions were used. A solution of cobalt $5 \times 10^{-3} \text{ mol.L}^{-1}$ in water and an aqueous solution of cobalt $5 \times 10^{-3} \text{ mol.L}^{-1}$ and dicyanamide 1 mol.L^{-1} was obtained by dissolving cobalt sulphate, sodium dicyanamide and water. By mixing different amounts of the two stock solutions in a quartz cell, solutions containing a constant concentration of $5 \times 10^{-3} \text{ mol.L}^{-1} \text{ Co(II)}$ and concentrations of DCA^- varying from 0 to 1 mol.L^{-1} can be obtained. In the following, we define R as the ratio of the initial concentration of DCA^- over the initial cobalt concentration: $R = [\text{DCA}^-]_{\text{init}}/[\text{Co(II)}]_{\text{init}}$. For the aqueous samples of this work, R was thus in the range 0 to 200.

Preparation of solutions containing cobalt and dicyanamide ions in ionic liquid $[\text{C}_1\text{C}_4\text{Pyrr}][\text{NTf}_2]$ was also conducted starting from two stock solutions.

The first stock solution was prepared by dissolving $\text{Co(NTf}_2)_2$ and $[\text{C}_1\text{C}_4\text{Pyrr}][\text{DCA}]$ in $[\text{C}_1\text{C}_4\text{Pyrr}][\text{NTf}_2]$ in order to obtain a cobalt and dicyanamide concentration of respectively 8.2×10^{-4} and 4.13 mol.L^{-1} . The second stock solution results from the dissolution of $\text{Co(NTf}_2)_2$ ($8.2 \times 10^{-4} \text{ mol.L}^{-1}$) in $[\text{C}_1\text{C}_4\text{Pyrr}][\text{NTf}_2]$. A procedure similar to that detailed above in water was used for the sample preparation in the ionic liquid. Various amounts of the two stock solutions were added in a quartz cell. Unlike the metal concentration which remains constant at $8.2 \times 10^{-4} \text{ mol.L}^{-1}$, the concentration of DCA^- varied from 0 to 4.13 mol.L^{-1} resulting in R ranging from 0 to 5040. Note that this protocol was also attempted with a higher concentration of cobalt, namely $5 \times 10^{-3} \text{ mol.L}^{-1}$ but a blue precipitate appeared when the R ratio was superior to 1. The formation of a solid powder has disrupted the UV-vis measurements and forced us to decrease the metal concentration.

All experiments were carried out at 20 °C. A vigorous stirring of all ionic liquid solutions was performed in the quartz cell for a period of 5 to 15 min. Several UV-Vis spectra were recorded until no modification between spectra recorded at successive time intervals was observed. In the following, only the last UV-vis spectrum has been considered.

2.3 Data fitting

A complexation chemical model between Co(II) and DCA⁻ ions was proposed and used to derive a theoretical mathematical expression of the absorbance at a fixed wavelength (see section 4.1) as a function of R. This theoretical expression was fitted to the experimental data by use of a home-written Fortran routine, implemented in the MINUIT facilities (CERN Librairies) based on a least square minimization procedure. The χ^2 convergence criterion was defined as:

$$\chi^2 = \frac{[\sum(A_{cal}-A_{exp})^2]^{\frac{1}{2}}}{(N_{dp}-N_{par})} \quad (1)$$

Where A_{cal} and A_{exp} are the theoretical and experimental absorbance values, respectively. N_{dp} and N_{par} represent the number of data points and the number of parameters respectively.

2.4 Extraction of cobalt

Firstly, starting from 0.7 mL solutions containing 5×10^{-3} mol.L⁻¹ of cobalt and 0 to 1 mol.L⁻¹ of sodium dicyanamide in water, 0.7 ml of [P₆₆₆₁₄][DCA] was added. The [DCA]/[Co] ratio of all solutions before extraction was of 0, 1, 3, 10, 20, 50, 100, 150 and 200 in the aqueous phase. Secondly, 0.7 mL of mixtures containing [P₆₆₆₁₄][DCA] and [P₆₆₆₁₄][NTf₂] were prepared to extract 5×10^{-3} mol.L⁻¹ of cobalt in an aqueous solution containing 1 mol.L⁻¹ of sodium

dicyanamide. The weight percentages of [P₆₆₆₁₄][DCA] in [P₆₆₆₁₄][NTf₂] were 0, 25, 50, 75 and 100 wt %.

After stirring and centrifugating the samples during 60 and 15 min respectively, the two phases were separated. The bottom aqueous phase was analysed before and after extraction by Atomic Absorption Spectroscopy (AAS). The extraction efficiency was measured thanks to the distribution coefficient (D) described in the following equation:

$$D = \frac{[Co]_0 - [Co]_f}{[Co]_f} \times \frac{V_{aq}}{V_{IL}} \quad (2)$$

[Co]₀ and [Co]_f correspond to the concentration of cobalt in the aqueous solution before and after extraction, respectively. V_{aq} is the volume of the aqueous phase and V_{IL} stands for the volume of the ionic liquid phase. According to experimental setup, the distribution coefficients are given with an error of ± 5 %.

2.5 Measurements

UV-vis spectra were recorded using a Cary 50 (Varian) spectrometer with a 1 cm wide quartz cell. Acquisition of all data was performed in the wavelength range of 200 to 800 nm. Pure water and neat [C₁C₄Pyrr][NTf₂] were used as reference samples for the aqueous and the ionic liquid mixtures, respectively. According to the accuracy of the absorbance given by the UV-vis spectrometer (± 5×10⁻³), and to our protocol, we can infer that the molar extinction coefficients are calculated in water and in the ionic liquid with an accuracy of ± 6 and ± 1 L.mol⁻¹.cm⁻¹ respectively.

The water content of the two ionic liquids was determined by using a Titroline® 7500 KF Trace (SI Analytics Karl Fisher). Hydranal® water standard 1.0, containing 1000 ppm of water was used for the device calibration, and results are the average of three measurements. Once dried as

described above, [C₁C₄Pyrr][NTf₂] and [C₁C₄Pyrr][DCA] were found to contain 35 ± 2 and 82 ± 5 ppm of water, respectively.

Atomic Absorption Spectroscopy was used to measure cobalt concentrations thanks to a PinAAcle 900F (Perkin Elmer) apparatus. Cobalt standards were prepared in the range 1 to 100 mg.L⁻¹. The working wavelength was set to 240.73 nm.

3) RESULTS

3.1 Co(II) in presence of DCA in water

In aqueous solution, cobalt(II) sulphate exhibits a light pink colour, due to the formation of a hexaaquocobalt(II) complex. Because of the weak complexation constant of the sulphate anion with cobalt(II),^[35] we can infer that the sulphate anion will not disrupt the complexation of cobalt in our conditions. The molar extinction coefficient versus the wavelength of an aqueous solution of 5×10^{-3} mol.L⁻¹ Co(II) sulphate is shown in Fig. 1a and was obtained by dividing the absorbance of the UV-vis spectrum by the initial concentration of cobalt. A maximum absorption peak centred around 509 nm and exhibiting a molar extinction coefficient of 4.80 L.mol⁻¹.cm⁻¹ is observed. A shoulder can be found at 480 nm and no significant absorbance is detected between 600 and 700 nm. This spectrum is in agreement with several previous experimental reports.^[26,36] The Tanabe-Sugano diagram of cobalt(II) hexahydrate, which predicts three spin-allowed transitions,^[36] is in line with our data for the maximum absorption and the shoulder, while the third predicted peak belongs to the near IR range, as indicated below:

$${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F) \text{ 1250 nm (near IR)}$$

$${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F) \text{ 510 nm (maximum absorption)}$$

$${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F) \text{ 463 nm (shoulder)}$$

Owing to a very low molar extinction coefficient value in the range 450 – 675 nm (for example, $\epsilon = 1.4 \times 10^{-3} \text{ L.mol}^{-1}.\text{cm}^{-1}$ at 509 nm), the addition of up to 1 mol.L⁻¹ of DCA⁻ has no influence on the baseline in this wavelength range. By contrast, below 450 nm, the DCA⁻ spectrum displays a clear increase in absorption. Absorbance of all UV-vis spectra in figure 1b thus strongly increases because of the impact of the extinction coefficient of the ligand below 450 nm. A UV-vis spectrum of an aqueous solution of 1 mol.L⁻¹ DCA is shown in supplementary materials to highlight this phenomenon. However, absorbance of the dicyanamide anion under 450 nm has a low impact on our modelling, because the latter was performed at higher wavelengths.

The molar extinction coefficients versus the wavelength for all 18 aqueous solutions containing varying concentrations of DCA⁻ are displayed in Fig. 1b. A maximum absorption peak and a shoulder are still observed at 509 and 480 nm respectively whatever the *R* value. No major wavelength shift between the different [DCA⁻]/[Co(II)] ratios is observed. Nevertheless, absorbance increases with the increasing *R* ratio. Furthermore, two shoulders at 595 and 645 nm appear when dicyanamide anion is added to the aqueous solution (see fig. 1a for comparison). These two experimental facts are a clear evidence of a complexation process between Co(II) and DCA⁻ in water.

3.2 Co(II) in presence of DCA in [C₁C₄Pyrr][NTf₂]

As stated previously in this article, a first attempt at studying the speciation of Co(II) in [P₆₆₆₁₄][DCA] revealed the presence of impurities that were influencing the speciation of Co(II). Because [C₁C₄Pyrr][NTf₂] and [C₁C₄Pyrr][DCA] were of a high purity grade, the latter was used in order to study the speciation of Co(II) in ionic liquid mixtures. Because neat [C₁C₄Pyrr][NTf₂]

was found to absorb significantly between 200 and 400 nm, molar extinction coefficients are only shown at wavelengths higher than 400 nm. As observed in an aqueous phase, the solution of $[C_1C_4Pyrr][NTf_2]$ containing only $Co(NTf_2)_2$ salt exhibits a light pink colour. The corresponding curve, presented in Fig. 2a($R = 0$), exhibits a maximum absorption wavelength at 506 nm with a molar extinction coefficient of $1.22 \text{ L.mol}^{-1}.\text{cm}^{-1}$. A shoulder can also be spotted at 460 nm. The dissolution of cobalt in another $[NTf_2]^-$ based ionic liquid namely 1-butyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)imide, $[C_1C_4Im][NTf_2]$ was already investigated and led to a similar spectrum.^[31] After drying the IL, the remaining amount of water was found to be three times lower than the amount of cobalt. In this study, we thus assume that water does not interfere in the complexation of cobalt by $[NTf_2]^-$. Because whether in an aqueous solution or in a NTf_2 -based ionic liquid, cobalt(II) is solvated by six oxygens leading to an octahedral complex,^[31,36] it presents similar molar extinction coefficients in these solvents.

The molar extinction coefficients versus the wavelength obtained for all 27 solutions of $[C_1C_4Pyrr][NTf_2]$ containing $Co(II)$ and various concentrations of DCA^- are plotted in Fig. 2b.

Starting from the solution without DCA^- , adding a small amount of dicyanamide, for instance $R = 0.1$, leads to a drastic change in the absorbance spectrum. The characteristic peaks of cobalt at 506 and 460 nm in $[C_1C_4Pyrr][NTf_2]$ are no longer observed. At this ratio, two major peaks can be seen at 589 and 602 nm with molar extinction coefficients of respectively 38.70 and $40.33 \text{ L.mol}^{-1}.\text{cm}^{-1}$. Two shoulders can also be observed at 569 and 624 nm. A hypsochromic shift of the two major peaks is highlighted when the ratio $[DCA^-]/[Co(II)]$ is increasing to $R = 25$. Indeed, for this ratio, the two previous absorption peaks are shifted towards 594 ($\epsilon = 521.8 \text{ L.mol}^{-1}.\text{cm}^{-1}$) and 613 nm (ϵ

= 527.2 L.mol⁻¹.cm⁻¹). From $R = 0$ to $R = 25$, the molar extinction coefficients of all spectra were found to increase and the solution changed from an initial light pink colour to a strong blue colour.

When R increases from 25 to 5040, ϵ drops drastically. The strong blue solution has now a light purple colour as seen in figure 2b. When the ratio $[DCA^-]/[Co(II)]$ is of 5040, one major peak can be observed at 597 nm with a molar extinction coefficient of 56.41 L.mol⁻¹.cm⁻¹ and two shoulders can be spotted at 569 nm and 655 nm. As observed in an aqueous solution, modifications of the UV-vis spectra with the increasing concentration of DCA^- are solid evidence of the complexation of Co(II) by dicyanamide anions in an ionic liquid.

3.3 Comparison of the two solvents

In a nutshell, for $R = 0$, molar extinction coefficients of cobalt in water and in an NTf₂-based IL are rather similar, as seen in Figs. 1a and 2a, respectively. As soon as $R > 0$, the speciation of cobalt(II) in an aqueous solution differs significantly from that observed in an ionic liquid, as revealed by the the UV absorption spectra collected in Figs. 1b and 2b.

The analysis of these UV-vis spectra can be refined by examining at a given wavelength, the variation of the experimental absorbance as a function of R . To that end, for each solvent, the wavelength exhibiting the highest variation in absorbance was first chosen. This corresponds to 509 and 613 nm for aqueous and ionic liquid phases, respectively. Then, the absorbances at these specific wavelengths were plotted against ratio R . These curves are presented in figures 3 and 4 in water and in [C₁C₄Pyrr][NTf₂], respectively. In the latter, the x-axis is represented in a logarithmic scale. In water, the increase in absorbance with R confirms the occurrence of a complexation

process. Because no plateau is observed even at $R = 200$, we can infer that the complexation of Co(II) is not complete. However, one can assume the presence of at least one complex of Co-DCA exhibiting a molar extinction coefficient significantly larger than that of the “free” cobalt ion in water. Regarding the ionic liquid, the curve’s trend displayed in figure 4 is more complex and clearly shows features that were previously difficult to highlight when looking at the entire UV-vis spectra. First, the absorbance increases from $R = 0$ to 0.8. Between $R = 0.8$ and $R = 2$, a narrow plateau is observed. Absorbance then increases again until $R = 25$ before reaching a maximum. Finally, above $R = 75$, absorbance decreases. This implies that several complexes of Co-DCA exist in the IL solution depending on the R value: one dominating the speciation from $R = 0$ to 0.8, a second one from $R = 25$ to 75 and a third one above $R = 75$. However, the narrow plateau observed in the range $R = 0.8-2$ is also indicative of (at least) one additional species, displaying a non-negligible contribution to the absorbance in that range.

The existence of several complexes is visually confirmed by the different colours observed in the solution with the increasing $[DCA^-]/[Co(II)]$ ratio. Note that the last complex dominating the speciation of Co(II) in the ionic liquid when R is superior to 1000 exhibits a very low absorbance.

3.4 Metal extraction

To highlight the importance of studying the speciation of Co-DCA in water, extraction of cobalt from an aqueous phase containing various $[DCA]/[Co]$ ratios with $[P_{66614}][DCA]$ was performed. Results are expressed in Figure 7. No extraction of metal was observed when cobalt was in an aqueous solution without any dicyanamide ion. However, the distribution coefficient (D) increases with the R ratio. Half of the cobalt is extracted at $R = 3$ ($D = 1$). A quantitative extraction of metal is observed for $R \geq 100$ leading to a distribution coefficient of 105. The influence of the DCA-NTf₂ ionic liquid mixtures on the extraction of Co(II) was studied using ionic

liquid mixtures containing 0, 25, 50, 75 and 100 wt % $[P_{66614}][DCA]$ in $[P_{66614}][NTf_2]$. Results are shown in Figure 8. $[P_{66614}][NTf_2]$ ionic liquid is unable to extract cobalt as the distribution coefficient of such mixture is close to 0. However the higher is the percentage of dicyanamide, the more efficient is the extraction. The distribution coefficient is thus of 1.4 and 105 for mixtures of 25 and 100 wt % of $[P_{66614}][DCA]$ in $[P_{66614}][NTf_2]$ respectively. One should notice that the density of $[P_{66614}][NTf_2]$ is of 1.11 and is higher than the one of the aqueous phase while the density of $[P_{66614}][DCA]$ is much lower, namely 0.89. This results in a phase inversion. The organic phase is thus the bottom phase from 0 to 25 wt % and is the top phase from 50 to 100 wt %.

4) DISCUSSION

4.1 Modelling of the complexation of a metal by a ligand

In this part, and because the analysis of Fig. 4 suggested the presence of complexes of Co(II), a general chemical and mathematical model expressing the successive complexations of cobalt by a ligand in a solvent is presented. Because the previous reports demonstrated the ability of cobalt to form up to four nitrogen-metal bounds in various complexes,^[37,38] this model involves one Co(II) “free” ion, the ligand, denoted L in the following, and successive $[Co(II)L_n]^{(2-n)-}$ complexes. In order to get chemical equations and mathematical expressions as general as possible and applicable to both water and ionic liquid systems, complexes $[Co(II)L_n]^{(n-2)-}$ were given the same general notation, that is X_n , with n indicating the number of DCA^- complexed around the central cation. Because the presence of water or of NTf_2^- anions around Co(II) are not explicitly described using this notation, it clearly does not reflect the exact composition of the first (and second) coordination sphere of Co(II) in water or in IL. It is however correct from a mathematical point of view, since the change of complexation appears to be directly correlated to the increase in the

DCA⁻ ion concentration in a solution of cobalt. In addition, the presence of water or NTf₂⁻ anion initially complexing Co(II) does not change the validity of the treatment presented here. As n increases in water, that is, as DCA⁻ anions enter the coordination sphere of Co(II), one can reasonably expect some water to be removed from the first coordination sphere. In an ionic liquid, because it is not clear whether NTf₂⁻ will form monodentate or bidentate bonds with Co(II), one can not ascertain how many NTf₂⁻ anions are removed from the coordination sphere of Co(II) as one DCA⁻ enters it. The notation chosen here is therefore, in our opinion, the one that is the most acceptable considering the lack of specific knowledge on the speciation of Co(II) in a neat ionic liquid.

The general chemical equation (1) describing the formation of successive complexes of Co(II) with a ligand L can thus be written as follows:



with $n = 0$ to 3 in this case. The stepwise complexation constant, K_{n+1} , can then be written as

$$K_{n+1} = \frac{[X_{n+1}]}{[X_n][L]} \quad (4)$$

where $[X_n]$ and $[L]$ denote the concentrations of the metal species and the ligand respectively.

In the absence of experimental values for the activity coefficients for the aqueous solutions of Co(II) and DCA⁻ ion, and because the concentration of ions are relatively low, we considered the solutions to behave ideally. Furthermore, because in the ionic liquid phase, our experimental protocol leads to a simple replacement of NTf₂⁻ by DCA⁻ ions, both having the same charge, the ionic strength can be considered to remain equal, and the activity coefficients to be constant. K_n in water and in the ionic liquid are thus ideal and conditional constants, respectively.

At any wavelength, the absorbance A can be described using the Beer-Lambert's law:

$$A = \sum_n \varepsilon_n [X_n] l + \varepsilon_L [L] l \quad (5)$$

where ε_n and ε_L stand for the molar extinction coefficients for species X_n and ligand L , respectively, and $[X_n]$ and $[L]$ correspond to the concentration of these species, respectively. l is the cell width expressed in cm. As explained above, the experimental values for the absorbance A were recorded at 509 or 613 nm in water or IL accordingly.

The set of equations represented by the general equations (3) and (5) are solved as a function of the complexation constant and the molar extinction coefficients using the mass conservation law for Co(II) and the ligand. For clarity reasons, details on the analytical expressions employed for solving this mathematical system are given in the supporting information.

In each solvent, the model parameters (K_n , ε_{Xn} and ε_L) are adjusted in order to describe the experimental absorbance values A by minimizing the χ^2 criterion (see eq. (1)).

4.2 Speciation of Co(II) in water

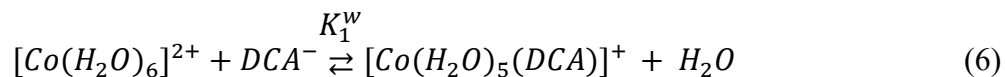
Based on the data presented in Fig. 3, we first assumed the simplest complexation scheme, by limiting the chemical model developed in section 4.1 to the formation of one complex only named X_1 . Under this hypothesis, the complexation constants K_2 , K_3 and K_4 and the molar absorption coefficients ε_2 , ε_3 and ε_4 are all set to 0. The number of parameters is thus reduced to 4, ε_O^w , ε_L^w , ε_1^w and K_1^w with the superscript w standing for water.

The adjusted values for the four parameters used within this model are listed in Table 1. Calculated values for the absorbance at 509 nm are plotted in Fig. 3 with respect to the ratio R . The fitted molar extinction coefficient of the metal $\varepsilon_O^w = 4.56 \text{ L.mol}^{-1}.\text{cm}^{-1}$ is close to the experimental value of $4.80 \text{ L.mol}^{-1}.\text{cm}^{-1}$ at 510 nm reported in the literature^[36] and also very close to our experimental value of $4.80 \text{ L.mol}^{-1}.\text{cm}^{-1}$ at 509 nm. The low χ^2 value (7.8×10^{-4}) reflects the good accuracy of

the model, as can be seen in Figure 3. Such a value is much lower than the experimental uncertainty so there is no need to consider additional complexes of higher stoichiometries and this simple model accurately reflects the experimental data. A value of 20.5 is found for the formation constant K_1^w . This relatively low complex formation value confirms that a significant excess of dicyanamide compared to the concentration of cobalt is needed in order to form X_I , the single Co-DCA complex in water. The concentrations of the two different cobalt species, X_0 and X_I , as calculated within the model, are presented in Figure 5 with respect to the ratio R. The free metallic ion (X_0) is gradually consumed to form X_I . At $R = 10$, half of the cobalt reacts with the dicyanamide anion, compared to 96 % of the complex formed when $[DCA^-]/[Co(II)] = 200$. The complexation constant is a factor of ca. 15 higher than that obtained for chloride, $[Co(H_2O)_5Cl]^+$ which exhibits a formation constant of 1.34.^[39]

It is important to notice that our chemical model in water describes the complexation of dicyanamidocobalt(II) complexes but is unable to bring any information on the coordination sphere of all complexes without comparing with previous literature data. In water, the coordination of cobalt is well known, and because H_2O is a neutral ligand, the charge of the Co-DCA complex will only be influenced by the complexation of DCA^- which is well described by our chemical model.

According to previous literature reports, cobalt(II) hexahydrate is assumed to form a single complex of $[Co(H_2O)_5(DCA)]^+$ in water.^[27] V.H. Köhlner,^[27] reported a simple chemical model based on the following equation:



Equation 6 is in full agreement with our results and confirms the validity of our modelling approach.

4.3 Speciation of Co(II) in [C₁C₄Pyrr][NTf₂]

As discussed in section 3.3, the situation in the IL is very different from that in water. In this case and considering the non-monotonous behaviour of the absorbance with respect to the ratio R (see Fig. 4), several dicyanamidocobalt(II) complexes need to be taken into account. In order to describe the absorbance curve reported here in a better way, our general model was used in two different ways, assuming the presence of three or four complexes of cobalt(II) with dicyanamide.

In a first version of the description, the formation of three Co-DCA complexes was assumed. 8 independent parameters, denoted as K_m^{IL} , ε_n^{IL} and ε_L^{IL} , with m varying from 1 to 3 and n from 0 to 3 were thus adjusted. The superscript IL stands for the ionic liquid, as these parameters are used to describe the complexation of Co(II) in the ionic liquid. The molar extinction coefficient for the ligand in the ionic liquid, ε_L^{IL} , was neglected because [C₁C₄Pyrr][DCA] presents a very close absorbance to [C₁C₄Pyrr][NTf₂] in the range 500 to 800 nm (see supporting information). The increase in absorption observed below 500 nm, as seen in Fig. 2b had no influence on our model since the wavelength selected in the ionic liquid was 613 nm. Furthermore, the drastic decrease in absorption observed at high [DCA⁻]/[Co(II)] ratio implies that the last complex exhibits very low molar extinction coefficients between 400 and 800 nm. Consequently, ε_3^{IL} was approximated to 0, reducing the number of unknown parameters to 6.

In a second version of our model, an additional complex, namely X_4 , corresponding to Co(II) complexed with four dicyanamide anions, was taken into account. In this case, a total of eight parameters were then adjusted.

Fitted values of all parameters for the both version of our model are listed in Table 1, together with the corresponding χ^2 values. Figure 4 plots the calculated values for the absorbance at 613 nm against the ratio R in a logarithmic scale.

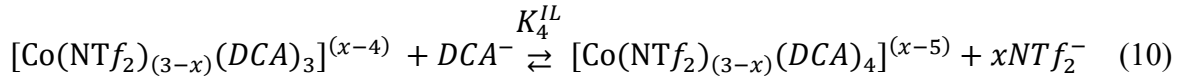
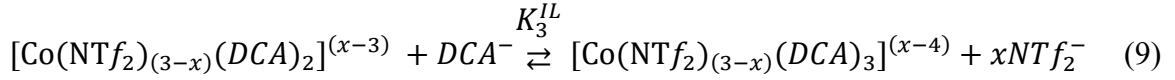
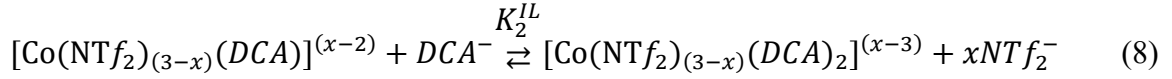
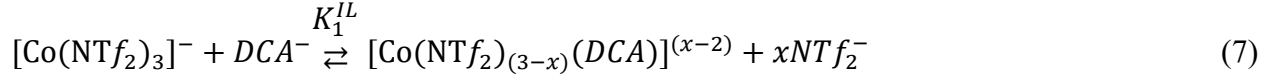
Regarding the first version of the model, that is considering only three cobalt(II) complexes, we observe that, on the one hand, the fit respects the trends of the experimental data from $R = 75$ to $R = 5040$. On the other hand, the calculated and measured absorbance values differ from $R = 0$ to $R = 50$. When the $[DCA^-]/[Co(II)]$ ratio is under 10, the calculated data is monotonously increasing and is not recovering the plateau observed experimentally between $R = 0.8$ and $R = 2$. Furthermore, the calculated molar extinction coefficient of cobalt(II) is of $14.42 \text{ L.mol}^{-1}.\text{cm}^{-1}$ whereas the experimental ϵ_0^{LL} is one order of magnitude lower ($\epsilon_0^{LL} = 1.22 \text{ L.mol}^{-1}.\text{cm}^{-1}$). Even if the χ^2 value appears to acceptable compared to the experimental uncertainty, the value for the calculated molar absorption of free Co(II) is too high and the shape of the curve from $R = 0$ to 10 is not completely satisfying. The assumption considering the presence of only three complexes, therefore, appears questionable.

Using the second version of the model based on four dicyanamidocobalt(II) complexes, (X_1 to X_4) the χ^2 now reaches a value of 3.7×10^{-3} , slightly lower than the value obtained when only three complexes are considered. Furthermore, calculated and experimental absorbance values are very close between $R = 0$ and 10. Strikingly, the local maximum observed between $R = 0.8$ to 2 is now accurately described. In addition, the calculated molar extinction coefficient of X_0 is now of $1.40 \text{ L.mol}^{-1}.\text{cm}^{-1}$, a value very close to the experimental one ($1.22 \text{ L.mol}^{-1}.\text{cm}^{-1}$) measured in this study. Taking into account four complexes thus appears to yield a significantly better description of the absorption data than those obtained when three complexes are considered.

The speciation of cobalt in an ionic liquid based on $[\text{NTf}_2]^-$ anion was recently studied.^[31] Authors revealed that Co(II) is surrounded by three bis(trifluoromethanesulfonyl)imide anions, yielding the formation of a monovalent negative complex $[\text{Co}(\text{NTf}_2)_3]^-$. The three NTf_2^- anions have been found to be bidentate, yielding a hexacoordinated Co(II) ion. In our study, Co(II) is thus assumed to be under the form of $[\text{Co}(\text{NTf}_2)_3]^-$ in neat $[\text{C}_1\text{C}_4\text{Pyrr}][\text{NTf}_2]$. According to our model, upon addition of dicyanamide anions into $[\text{C}_1\text{C}_4\text{Pyrr}][\text{NTf}_2]$, up to four DCA^- ions are expected to enter the solvation sphere of Co(II). However, because NTf_2^- can be either bidentate or monodentate,^[31] the exact number of such an anion surrounding Co(II) as DCA^- increases is not known. Therefore, the only valid general expression for describing the heteroleptic Co(II) complex in $[\text{C}_1\text{C}_4\text{Pyrr}][\text{NTf}_2]$ is $[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})_y]^{(x-y-1)}$ with x ranging from 0 to 3 and y from 0 to 4. Note that using this definition, the overall charge of the complex is supposed to be negative.

The spectroscopic data are thus accurately described within a model using five species, namely $[\text{Co}(\text{NTf}_2)_3]^-$ (X_0^{IL}), $[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})]^{(x-2)}$ (X_1^{IL}), $[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})_2]^{(x-3)}$ (X_2^{IL}), $[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})_3]^{(x-4)}$ (X_3^{IL}) and $[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})_4]^{(x-5)}$ (X_4^{IL}). x represents the number of bis(trifluoromethylsulfonyl)imide that will be replaced by dicyanamide anions during the complexation of cobalt. Each chemical entity has a specific molar extinction coefficient, denoted respectively ε_0^{IL} , ε_1^{IL} , ε_2^{IL} , ε_3^{IL} and ε_4^{IL} . The formation of these four complexes is governed by four complexation constants (K_1^{IL} , K_2^{IL} , K_3^{IL} and K_4^{IL}).

The version of our chemical model assuming four Co-DCA complexes can thus be written as follows:



Values of 1.73×10^6 , 2.71×10^4 , 6.30×10^2 and 3.65 are obtained as the complexation formation constants K_1^{IL} , K_2^{IL} , K_3^{IL} and K_4^{IL} are obtained, respectively. Due to a strong complexation constant, the first two complexes are likely to form at $R < 3$ unlike the fourth and last Co-DCA complex that will be observed only in the presence of a large excess of dicyanamide anions.

Fig. 6 then displays the speciation diagram calculated using the four K_4^{IL} discussed above. The variation of species concentration in the ionic liquid (in mol. %) is plotted against the ratio R . The concentration of $[\text{Co}(\text{NTf}_2)_3]^+$ decreases rapidly, reaching 0.1 % at $R = 2$. The first complex $[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})]^{(x-2)}(X_1^{IL})$ reaches its maximum in the ionic liquid at $R = 1$ (80.0 %). It then disappears when $R = 2$ (4.0 %) to the benefit of the second complex $[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})_2]^{(x-3)}(X_2^{IL})$ which reaches its maximum at the same ratio (68.7 %). Regarding the third complex $[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})_3]^{(x-4)}(X_3^{IL})$, a continuous growth of the concentration can be observed from $R = 1$ to $R = 25$ with a molar percentage of respectively 0.03 and 86.7 %. However X_3^{IL} fades away from a ratio $[\text{DCA}^-]/[\text{Co}(\text{II})]$ superior to 25. The last complex, namely $[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})_4]^{(x-5)}(X_4^{IL})$ appears

at $R = 3$ and slowly grows until reaching a value of 93.8 % at $R = 5040$. When the $[DCA^-]/[Co(II)]$ reaches 5040, there is 6.2 % of X_3^{IL} remaining in the solution.

Overall and as expected, dicyanamide anion appears to be a significantly stronger ligand than NTf_2^- . The gradual addition of DCA^- in the coordinating sphere of $Co(II)$ rather than an immediate formation of tetracyanamidocobaltate(II) complex is due to the high concentration of NTf_2^- in the ionic liquid. Besides, K_1^{IL} is ca. five orders of magnitude higher than the value for the formation constant of $[Co(H_2O)_5(DCA)]^+$ obtained in water ($K_1^w = 20.5$), while K_2^w , K_3^w and K_4^w are null in water. We, thus, can infer that bis(trifluoromethylsulfonyl)imide is a weaker ligand of cobalt than water, a statement that is confirmed by numerous evidences already reported in the literature.^[31,40]

4.4 Geometry of the complexes

According to the crystal field theory, molar extinction coefficient of transition metal complexes can drastically change with the geometry of the compound.^[36,41,42] In the case of cobalt(II), low values of ϵ , namely under $100 L \cdot mol^{-1} \cdot cm^{-1}$ can be linked to an octahedral geometry,^[27] as observed for $[Co(H_2O)_6]^{2+}$ ($\epsilon = 4.5 L \cdot mol^{-1} \cdot cm^{-1}$). A higher extinction coefficient value is most probably due to a tetrahedral geometry as observed with $CoCl_4^{2-}$ that exhibits a molar extinction coefficient of $615 L \cdot mol^{-1} \cdot cm^{-1}$ at 690 nm in water.^[36] This phenomenon is explained by the inversion centres observed in octahedral complexes that leads to forbidden transitions according to the Laporte law.^[41,41,43] Our study indicates that the complex containing three dicyanamide anions in the ionic liquid exhibits a molar extinction coefficient of $640 L \cdot mol^{-1} \cdot cm^{-1}$ and a strong blue color, while, adding extra DCA^- anions leads to a complex with an inversed centre and thus a negligible absorbance as derived from ϵ_{X4} values. We, thus, suggest that, in accordance with equation 10,

$[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})_3]^{(x-4)}$ is present in a tetrahedral geometry and becomes octahedral when one dicyanamide anion is added in order to form $[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})_4]^{(x-5)}$. This assumption is strengthened by recent papers dealing with the geometry of cobalt(II) complexes with thiocyanate anions in ionic liquid media.^[43,44] In this work tetrahedral complexes exhibit a strong blue colour while a bright red colour is observed for octahedral complexes.

4.5 From the speciation to the extraction

A strong correlation can be made between the speciation diagram of Co-DCA in water provided in Figure 5 and the extraction trend of cobalt with various $[\text{DCA}]/[\text{Co}]$ ratio in water. The $[\text{Co}(\text{H}_2\text{O})_5(\text{DCA})]^+$ complex predominates in water when the concentration of dicyanamide is 100 times higher than the concentration of cobalt. Similarly, the extraction of cobalt increases with the $[\text{DCA}]/[\text{Co}]$ ratio until reaching a plateau for $R \geq 100$. This result proves that cobalt needs to be under the form of a monodicyanamide complex in order to be extracted into $[\text{P}_{66614}][\text{DCA}]$. In other words, a dicyanamide IL is unable to extract the free metallic cobalt cation solvated in water. Furthermore, the nature of the organic phase also has a significant impact on the cobalt extraction. We reported that DCA ILs present a higher complexation constant of cobalt than what is observed in NTf_2 based ionic liquids or in water. This results in a more efficient extraction of Co(II) as the concentration of dicyanamide increases, as shown in Figure 7. It is important to notice that while cobalt is efficiently extracted from a dicyanamide aqueous medium, the colour of the metal changes from red in the aqueous phase before extraction to a strong blue colour in the ionic liquid. This is characteristic of a difference in complexation of Co(II) in water and in an IL, as demonstrated in this work. Cobalt(II) is, thus, in the form of a pink octahedral $[\text{Co}(\text{H}_2\text{O})_5(\text{DCA})]^+$ complex in water. Upon extraction towards the ionic liquid that contains a large amount of

dicyanamide ligands, the metal complex changes. According to the UV-Vis spectrum, Co(II) releases its water molecules, while three dicyanamide and one or two (NTf₂)⁻ anions complex the metal, leading to a blue [Co(NTf₂)_(3-x)(DCA)₃]^(x-4) compound. According to the speciation study reported here, it is expected that the apparition of the fourth and last complex, namely [Co(NTf₂)_(3-x)(DCA)₄]^(x-5) requires a huge excess of ligands compared to the metal and is thus unlikely to be predominant during liquid-liquid extractions. Finally, the exact mechanism, specifically whether the complex change occurs at the interface, or if [Co(H₂O)₅(DCA)]⁺ passes the interface and changes into [Co(NTf₂)_(3-x)(DCA)₃]^(x-4) within the ionic liquid is not yet established. Further experiments for elucidating the extraction mechanism are beyond the scope of the article and shall be carried out shortly.

5) CONCLUSIONS

We have investigated and compared the complexation of cobalt by dicyanamide in water and in an ionic liquid, [C₁C₄Pyrr][NTf₂]. Strong evidences showed that only one DCA⁻ is complexing [Co(H₂O)₆]²⁺ in order to form [Co(H₂O)₅(DCA)]⁺ in an aqueous solution. Due to a low complexation constant, a large excess of DCA ligand must be added to complex most of the cobalt in water. Regarding the ionic liquid, a model assuming four different complexes [Co(NTf₂)_(3-x)(DCA)]^(x-2), [Co(NTf₂)_(3-x)(DCA)₂]^(x-3), [Co(NTf₂)_(3-x)(DCA)₃]^(x-4) and [Co(NTf₂)_(3-x)(DCA)₄]^(x-5) which concentrations are directly related to the [DCA⁻]/[Co(II)] ratio is shown to be fully in line with the experimental data. This work underlines the fact that speciation of metal ions in an ionic liquid can be more exotic than that observed in water. In addition, not previously observed complexes, such as the [Co(NTf₂)_(3-x)(DCA)₃]^(x-4) and [Co(NTf₂)_(3-x)(DCA)₄]^(x-5), might show potentially promising physical or chemical properties. As far as liquid-liquid extraction is concerned, extraction mechanisms can thus be significantly influenced by the nature of the metal

complex formed within an ionic liquid. For instance, extraction of cobalt(II) using a mixture of hydrophobic ionic liquids based on NTf_2^- and DCA^- anion could very well enhance the extraction of this metal within the ionic liquid phase, due to the metal complexes formed with the dicyanamide anion. Optimisation of the metal ion extraction was obtained by carefully choosing the ratio of Co^{2+} , DCA^- and NTf_2^- anions in the aqueous and organic phase.

FIGURES

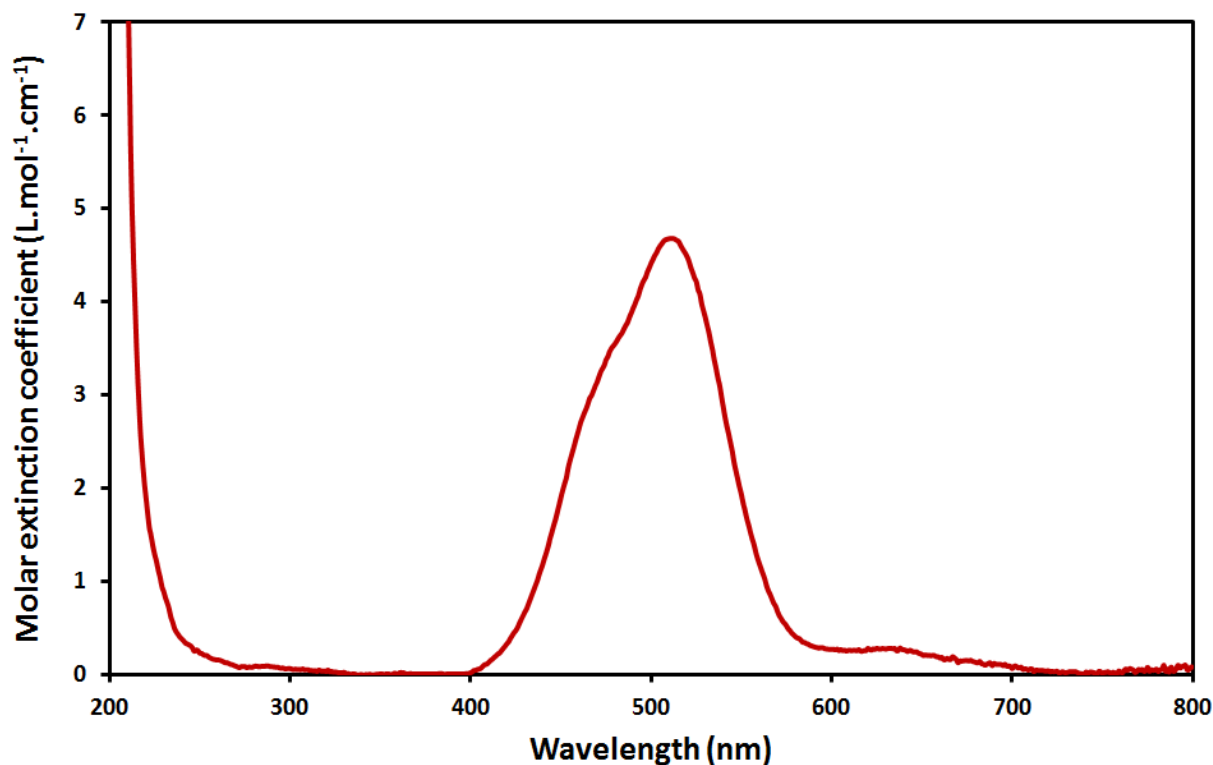


Figure 1a. Molar extinction coefficient of CoSO_4 in water versus the wavelength.

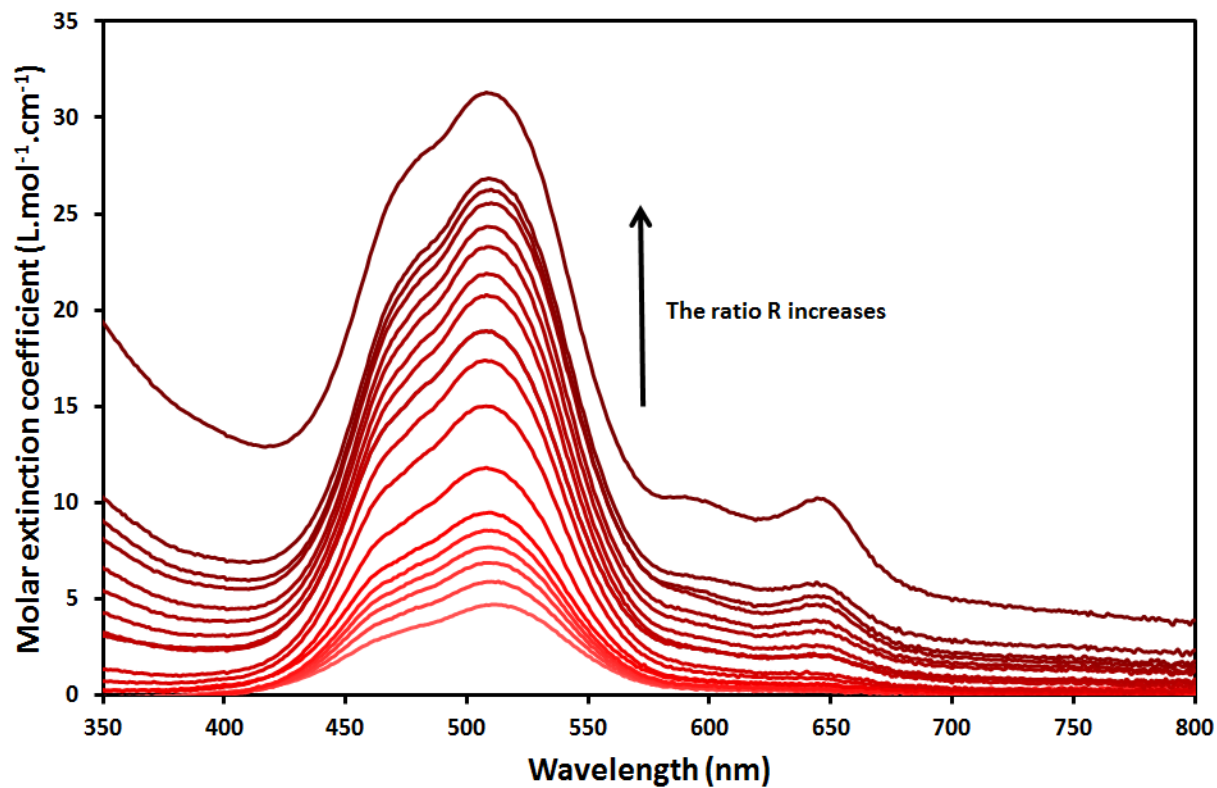


Figure 1b. Molar extinction coefficient for various $[\text{DCA}^-]/[\text{Co(II)}]$ ratios (0 to 200) in water versus the wavelength.

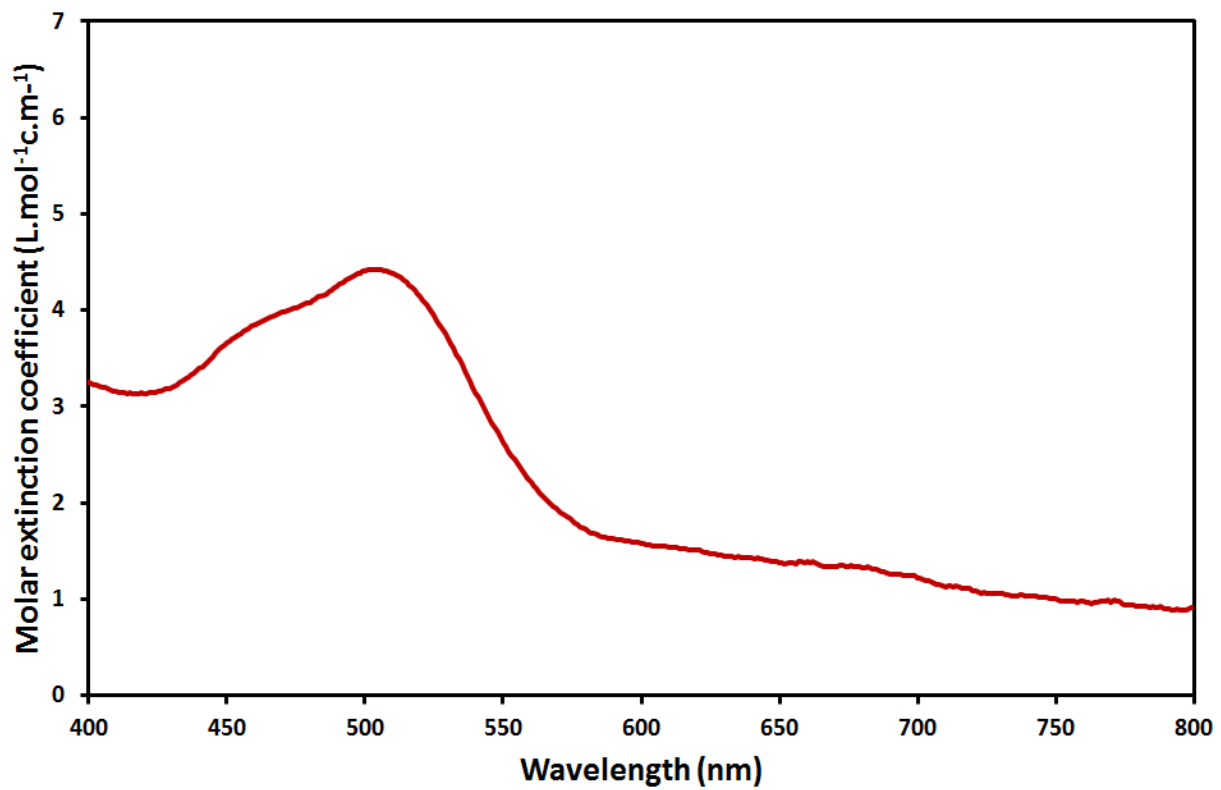


Figure 2a. Molar extinction coefficient of Co(NTf₂) in [C₁C₄Pyr][NTf₂] versus the wavelength.

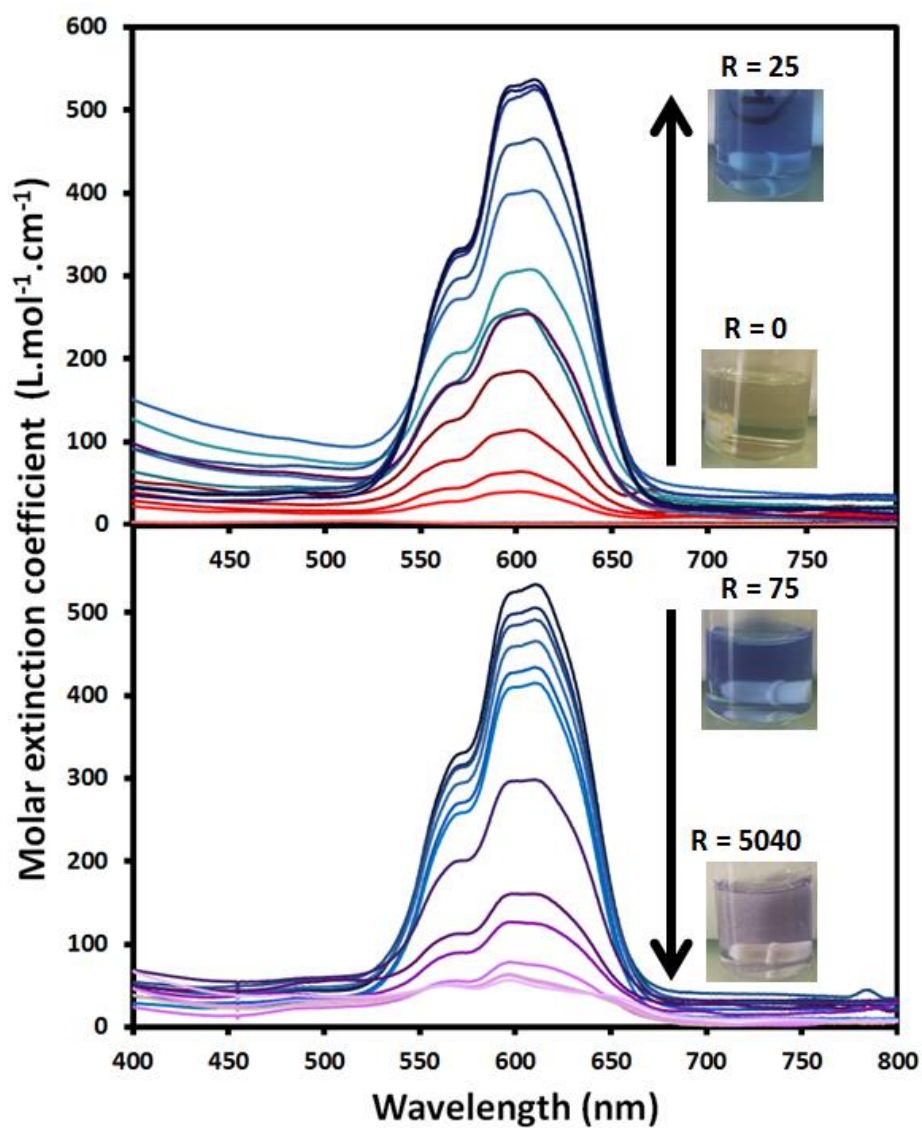


Figure 2b. Molar extinction coefficient of the solution for various $[\text{DCA}^-]/[\text{Co(II)}]$ ratios ($R = 0$ to 5040) in $[\text{C}_1\text{C}_4\text{Pyrr}][\text{NTf}_2]$ versus the wavelength.

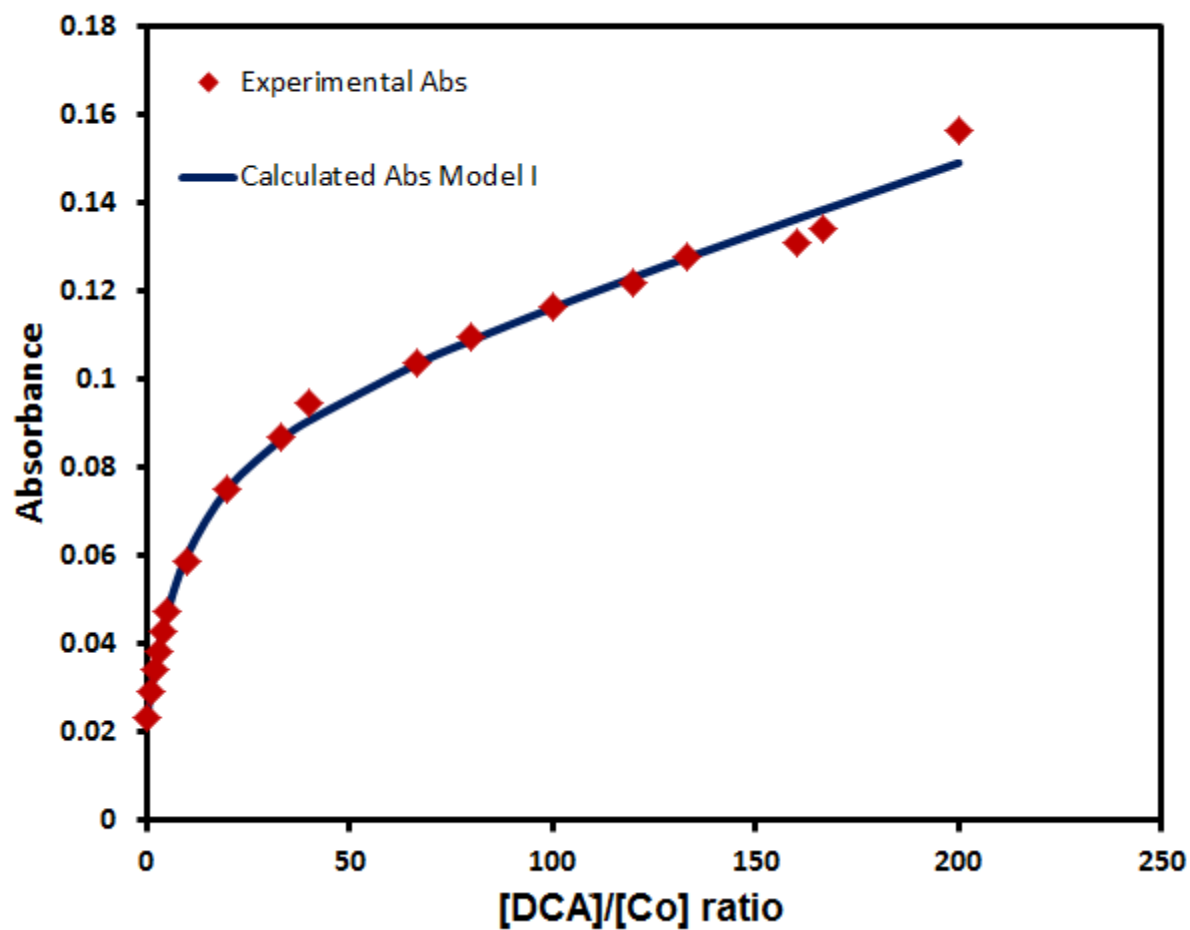


Figure 3. Experimental and calculated absorbance at 509 nm versus the R ratio (0 to 200) in water. Diamond: experimental points. Solid line: calculated data according to our model assuming one complex.

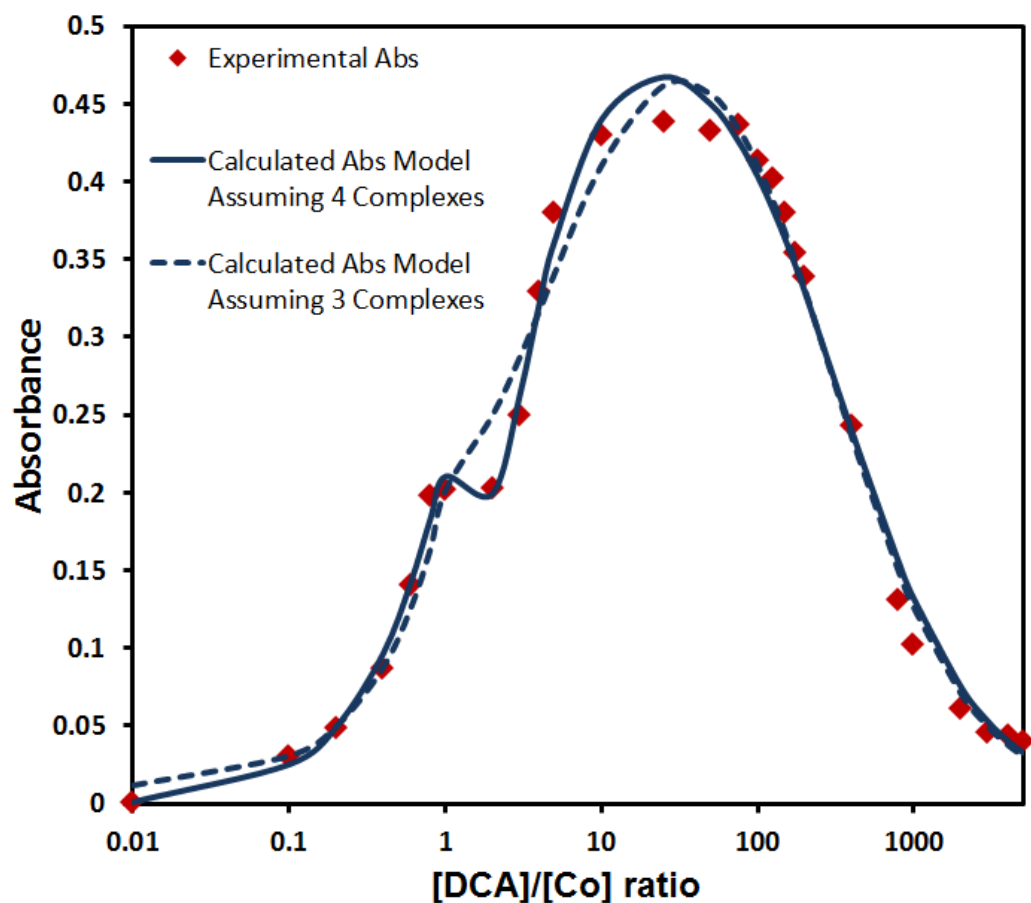


Figure 4. Experimental and calculated absorbance at 614 nm versus the R ratio (0 to 5040) in $[\text{C}_1\text{C}_4\text{Pyr}][\text{NTf}_2]$. Diamond: experimental points. Dashed line: calculated value according to our model assuming three complexes. Solid line: Calculated value according to our model assuming four complexes.

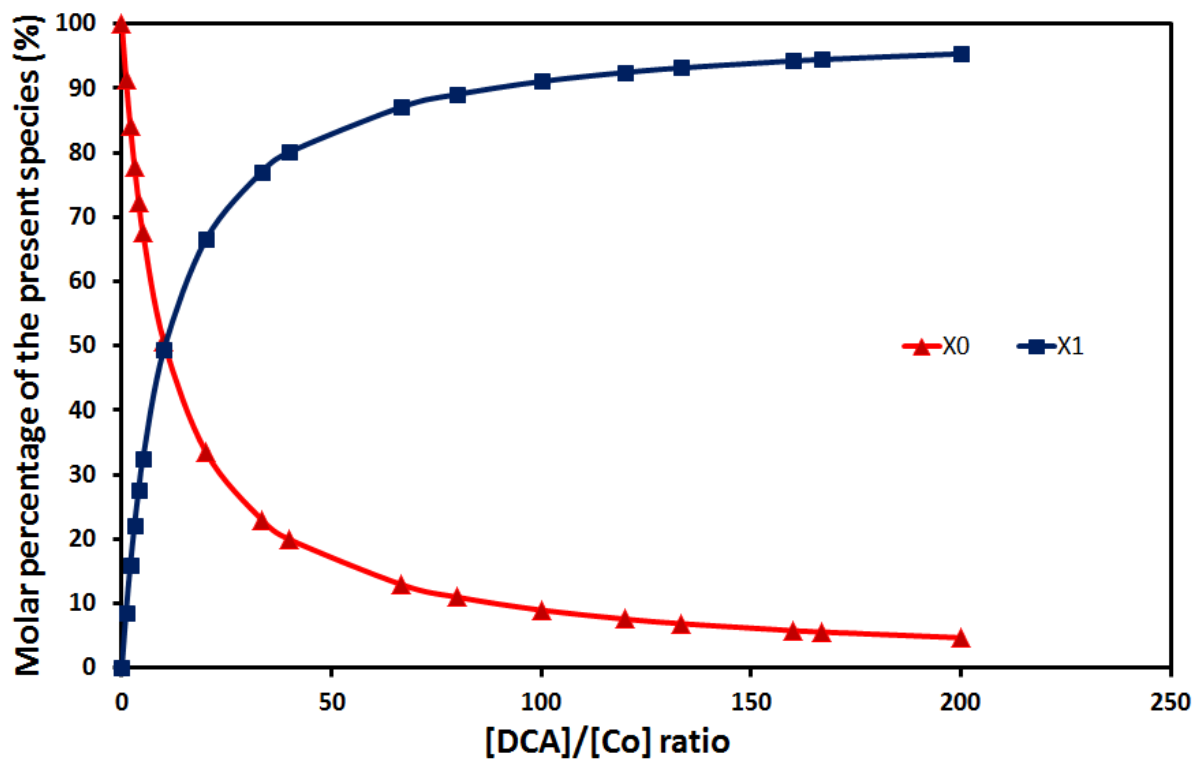


Figure 5. Chemical speciation for $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ (X_0) and $[\text{Co}(\text{H}_2\text{O})_5(\text{DCA})]^+$ (X_1) for each R ratio in an aqueous solution. Triangle: (X_0) concentration. Square: (X_1) concentration.

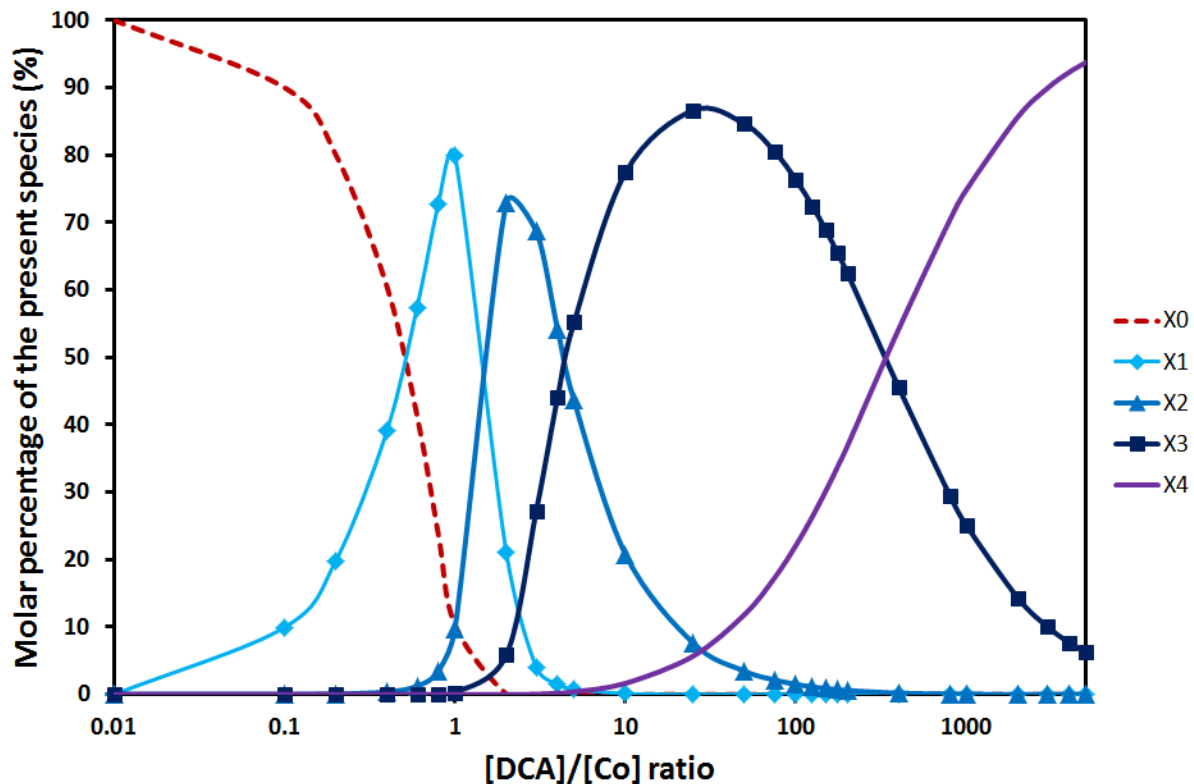


Figure 6. Chemical speciation for $[\text{Co}(\text{NTf}_2)_3]^+(X_0)$, $[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})]^{(x-2)}(X_1)$, $[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})_2]^{(x-3)}(X_2)$, $[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})_3]^{(x-4)}(X_3)$ and $[\text{Co}(\text{NTf}_2)_{(3-x)}(\text{DCA})_4]^{(x-5)}(X_4)$ for each R ratio in the ionic liquid. Dashed line: (X_0) concentration. Diamond: (X_1) concentration. Triangle: (X_2) concentration. Square: (X_3) concentration. Full line: (X_4) concentration.

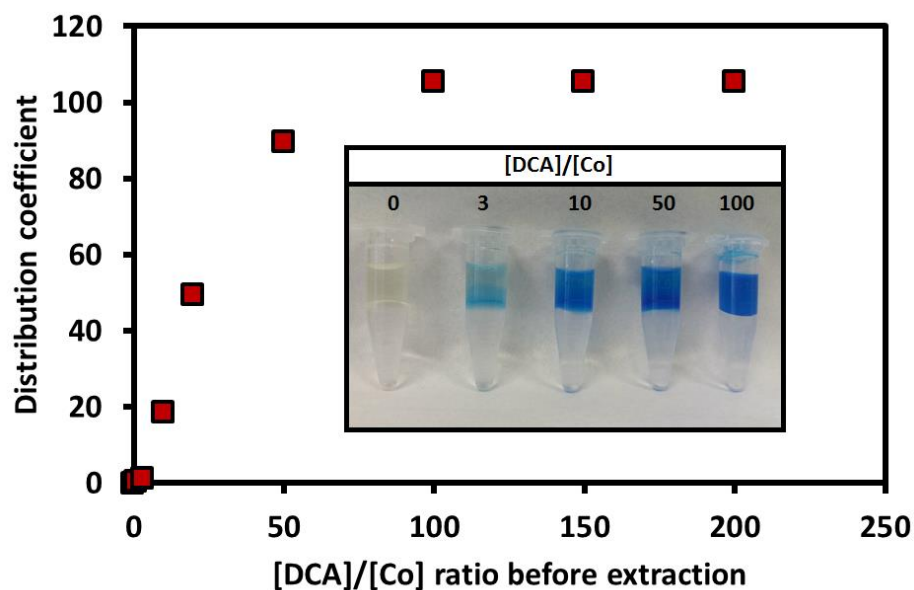


Figure 7. Extraction of cobalt 5.10^{-3} mol.L $^{-1}$ in water with $[P_{66614}][DCA]$ from an aqueous phase containing $[DCA]/[Co]$ ratios of 1, 3, 10, 20, 50, 100, 150 and 200. Snapshots of extraction at ratios of 0, 3, 10, 50, 100 are presented. Ionic liquid phase is on top.

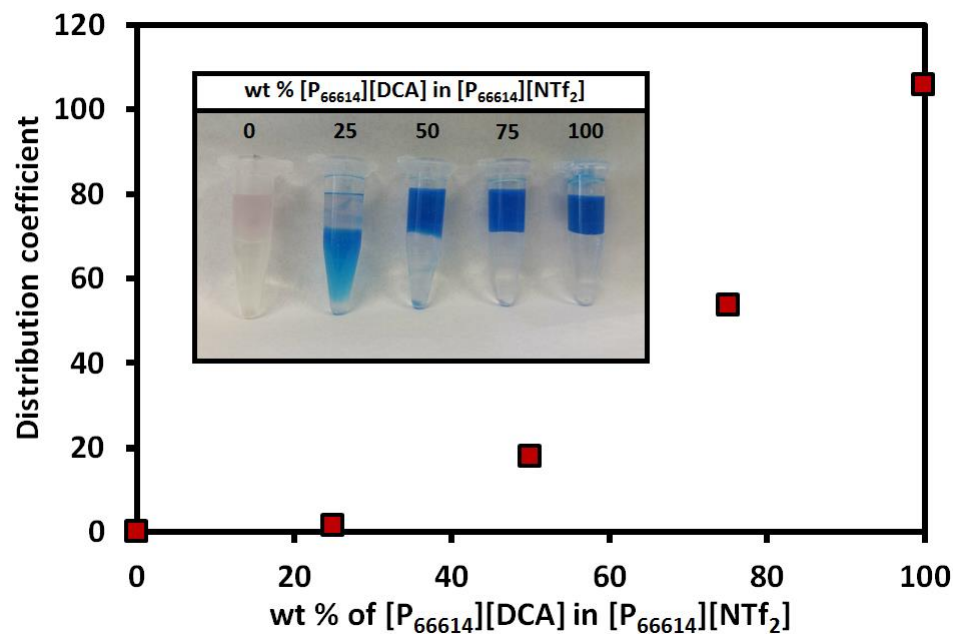


Figure 8. Extraction of cobalt 5.10^{-3} mol.L⁻¹ in water and 1 mol.L⁻¹ of sodium dicyanamide by [P₆₆₆₁₄][DCA]-[P₆₆₆₁₄][NTf₂] mixtures. Weight percentages of [P₆₆₆₁₄][DCA] are of 0, 25, 50 and 100 wt %. Snapshots of all extractions are presented. 0 and 25 wt % of [P₆₆₆₁₄][DCA]: Aqueous phase is on top . 50, 75 and 100% of [P₆₆₆₁₄][DCA], ionic liquid phase is on top.

TABLES

Complexation of cobalt by dicyanamide			
Parameters	Model assuming 1 complex in water	Model assuming 3 complexes in [C ₁ C ₄ Pyrr][NTf ₂]	Model assuming 4 complexes in [C ₁ C ₄ Pyrr][NTf ₂]
ϵ_0 (L.mol ⁻¹ .cm ⁻¹)	4.56± 1	1.44×10 ¹ ± 1.4×10 ¹	1.40± 1
ϵ_1 (L.mol ⁻¹ .cm ⁻¹)	1.86×10 ¹ ± 1×10 ¹	2.46×10 ² ± 1.5×10 ¹	2.97×10 ² ± 1.5×10 ¹
ϵ_2 (L.mol ⁻¹ .cm ⁻¹)	0	6.85×10 ² ± 1.5×10 ¹	1.95×10 ² ± 1.5×10 ¹
ϵ_3 (L.mol ⁻¹ .cm ⁻¹)	0	0	6.40×10 ² ± 1.0×10 ¹
ϵ_4 (L.mol ⁻¹ .cm ⁻¹)	0	0	0 ^a
ϵ_L (L.mol ⁻¹ .cm ⁻¹)	5.9×10 ⁻² ± 1×10 ⁻²	0	0
K_1	2.05×10 ¹ ± 5	9.15×10 ⁸ ± 1.0×10 ¹⁶	1.73×10 ⁶ ± 1.0×10 ⁶
K_2	0	2.18×10 ² ± 5.0×10 ¹	2.71×10 ⁴ ± 2.0×10 ⁴
K_3	0	4.23± 1	6.30×10 ² ± 5
K_4	0	0	3.65± 2×10 ⁻¹
χ^2	7.8×10 ⁻⁴	4.8×10 ⁻³	3.7×10 ⁻³

a: Value for ϵ_4 set to 0. See text for details.

Table 1. Calculated parameters for cobalt complexation by dicyanamide in an aqueous solution (Model assuming one complex) and in [C₁C₄Pyrr][NTf₂] (Model assuming three and four complexes).

ASSOCIATED CONTENT

Supplementary materials 1:

According to the law of the conservation of mass, initial concentrations of metal M^0 and ligand L^0 can be expressed as:

$$[X_0] + [X_1] + [X_2] + [X_3] + [X_4] = M^0 \quad (S1)$$

$$[L] + [X_1] + 2[X_2] + 3[X_3] + 4[X_4] = L^0 \quad (S2)$$

By combining equations (1), (S1) and (S2), M^0 , L^0 and K_n can be related in equation (S3):

$$A_0 L^5 + A_1 L^4 + A_2 L^3 + A_3 L^2 + A_4 L - A_5 = 0 \quad (S3)$$

Where A_0 , A_1 , A_2 , A_3 , A_4 and A_5 are defined by the following equations:

$$K_1 K_2 K_3 K_4 = A_0 \quad (S4)$$

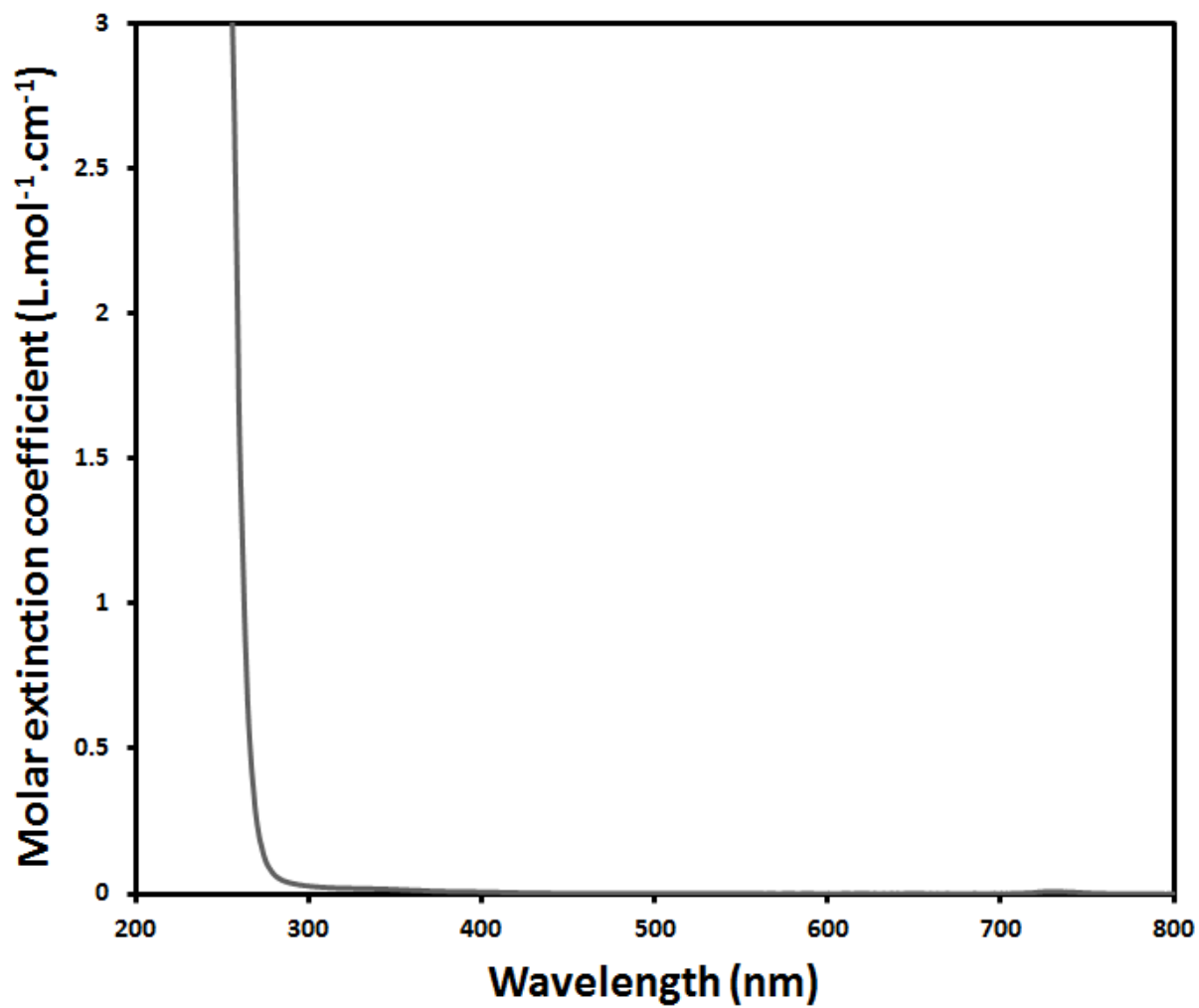
$$K_1 K_2 K_3 + K_1 K_2 K_3 K_4 (4M^0 - L^0) = A_1 \quad (S5)$$

$$K_1 K_2 + K_1 K_2 K_3 (3M^0 - L^0) = A_2 \quad (S6)$$

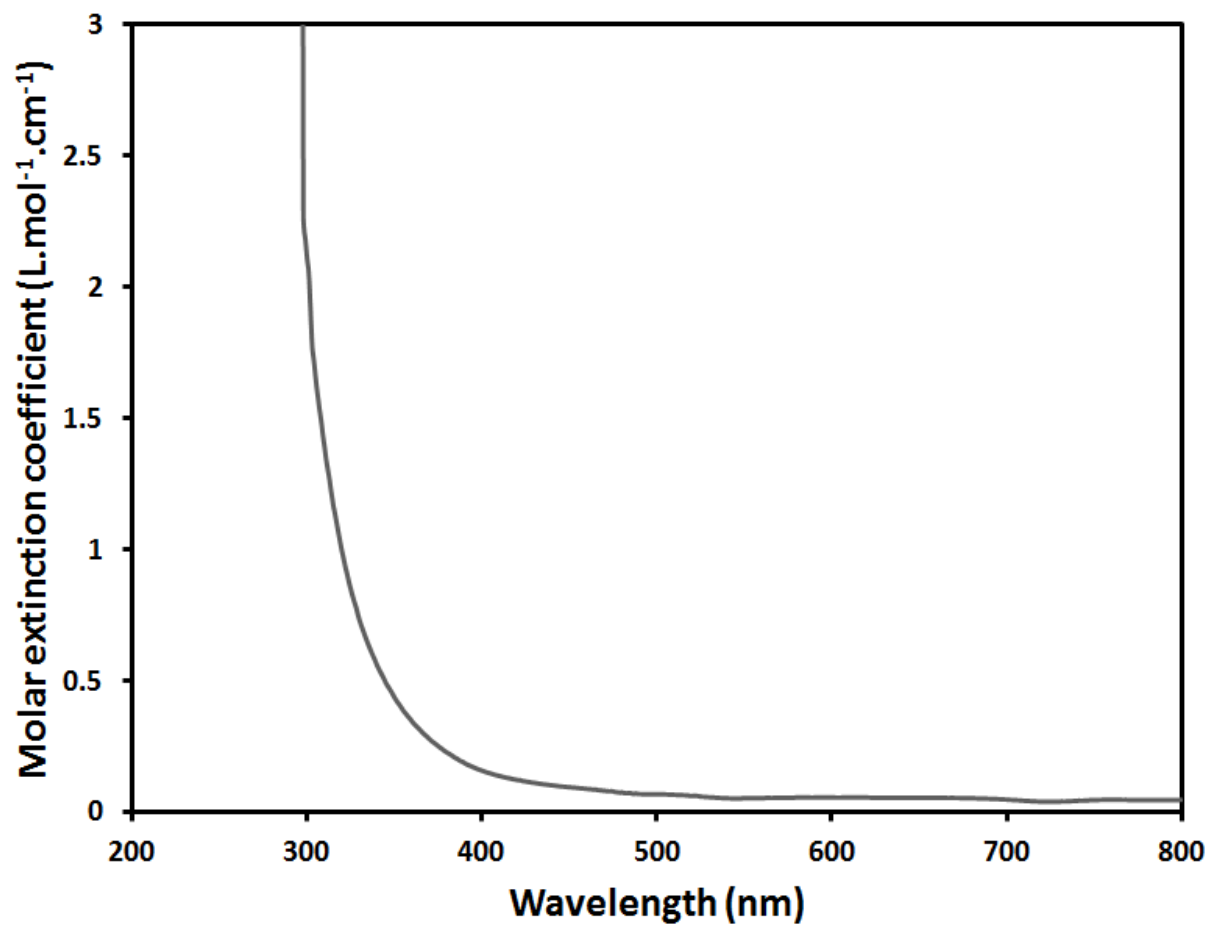
$$K_1 + K_1 K_2 (2M^0 - L^0) = A_3 \quad (S7)$$

$$1 + K_1 (M^0 - L^0) = A_4 \quad (S8)$$

$$L^0 = A_5 \quad (S9)$$



Supplementary materials 2. Molar extinction coefficient for sodium dicyanamide in water. Pure water was used as a reference sample.



Supplementary materials 3. Molar extinction coefficient for [C₁C₄Pyr][NTf₂]. No reference sample was used

NOTES

The authors declare no competing financial interest.

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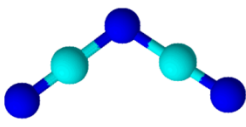
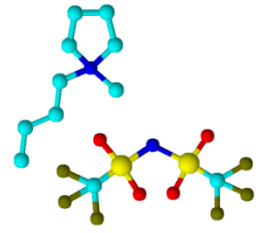
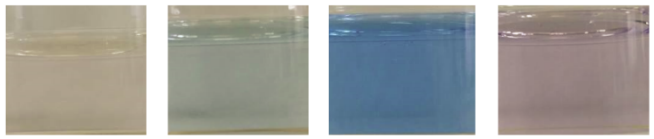
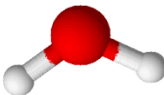

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GRAPHICAL ABSTRACT

		Dicyanamide concentration 	
Media	Metal		
$[\text{C}_1\text{C}_4\text{Pyrr}][\text{NTf}_2]$ 	Co^{2+}		
H_2O 	Co^{2+}		

New complexing ligands of cobalt need to be found in order to develop efficient recycling processes. UV-vis measurements and ad hoc modelling were applied to investigate the complexation of cobalt by dicyanamide in water and in an ionic liquid (IL). We report that the cation can complex very differently from an aqueous to an organic media. Speciation diagrams and complexation constants were calculated in detail. As a proof of concept, cobalt was extracted by an IL in a dicyanamide aqueous solution.

