

Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Thermochromism, stability and thermodynamics of cobalt(II) complexes in newly synthesized nitrate based ionic liquid and its photostability

Nemanja Banić, Milan Vraneš, Biljana Abramović, János Csanádi and Slobodan Gadžurić*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

In this work 1-(2-hydroxyethyl)-3-methylimidazolium nitrate ionic liquid, [HO(CH₂)₂mim]NO₃, have been synthesized in order to serve as a new thermochromic material upon addition of cobalt(II) ions. Spectrophotometric measurements of series of cobalt(II) nitrate and cobalt(II) chloride solutions in [HO(CH₂)₂mim]NO₃ at 298.15, 308.15, 318.15, 328.15, and 338.15 K were performed. Based on the recorded spectra, the overall stability constants and thermodynamic parameters for the cobalt(II) associations with chloride and nitrate ions were calculated. The thermodynamic calculations suggest that thermochromism is not observed in the ionic medium due to a small entropy changes during the replacement of nitrate ions with chlorides in the co-ordination sphere of cobalt(II). The absence of the molecular solvent was also the reason for the lack of thermochromism. Thus, cobalt(II) solutions in the [HO(CH₂)₂mim]NO₃ + water mixtures were studied as a new and green medium that can be used for the auto-regulation of the light intensity and shading protection. Investigated system with water upon addition of cobalt(II) was found to be far more efficient and responsive thermochromic medium of all studied systems up to now. The structure of [HO(CH₂)₂mim]NO₃ was confirmed by both ¹H NMR and IR spectroscopy. Also, the efficiency of different advanced oxidation processes (UV-induced photolysis, UV/H₂O₂ photolysis, heterogeneous photocatalysis by using TiO₂ Degussa P25 and TiO₂ with 7.24% w/w Fe catalysts) for the [HO(CH₂)₂mim]NO₃ degradation were investigated. The reaction intermediates formed during the photo-oxidation process were identified using the LC-ESI-MS/MS and ¹H NMR techniques.

Introduction

The possibility to combine thermally responsive chemical processes was studied in this work, in order to attain simultaneous control of temperature and light intensity in agricultural greenhouses and in residential field. Since the sunlight can be directly absorbed by many coloured substances to re-generate heat with achievable temperature below 373.15 K, it is increasingly important to develop new chemical systems that can store and utilize this almost free and readily available solar heat. Research work in this area involves studies of new materials and their optical properties upon addition of some thermochromic complex compounds. The thermochromic substance is usually transition metal, such as cobalt(II) with mixed ligands, undergoing reversible changes of optical properties in response to a change of temperature, acting thus, as a self-regulating shading.¹ Reversibility of the process may provide constant temperature in the residential buildings or agricultural greenhouses used for cultivation of some delicate plants in fluctuating climate conditions. Incorporated in the „smart windows“ this materials may cut energy use in the buildings in the near future, since the windows are significant source of energy loss.

The studies on the ionic association (complex formation) at an early stage have mainly been restricted to aqueous solutions as reaction media,^{2,3} but the irreversible water evaporation upon heating is a predictable problem that can shorten the life cycle of the thermochromic devices based on aqueous solutions. Several studies were oriented toward inorganic molten nitrates as a potential medium for thermochromic cobalt(II) halide complex formation,^{4,5} but disadvantage of molten salts was their high melting point, which was the main reason for their low applicability.

By addition of small amounts of a molecular solvent in anhydrous molten salts in order to decrease the melting point, a large number of suitable media in which cobalt(II) halide complexes show thermochromic behaviour were obtained.⁶⁻⁸ Studies have shown that cobalt(II) thermochromism strongly depends on the amount of added molecular solvent as well as its physical and chemical properties,^{9,10} but the reason why this effect occurs in these systems was not successfully explained. Also, it remained an open question whether thermochromic effect may occurs in systems that do not contain a molecular solvents, but that remains liquid at temperatures that are low enough for possible application in practice. Therefore, the nitrate based ionic liquids was imposed as the ideal answer to this question. Also, the influence of addition of the molecular solvent into room

temperature ionic liquid on cobalt(II) thermochromism was not investigated yet, although in our previous papers we already investigated and shown that the presence of the molecular solvent (e.g. water, lower amides, dimethylsulfoxide etc.) in the mixture with inorganic salts significantly improves cobalt(II) thermochromism.^{8–11}

Ionic liquids are the excellent solvent candidate due to their unique physical and chemical properties (e.g. negligible vapour pressure, low toxicity, non-corrosivity etc.) and thermochromic behaviour of chlorido nickel complexes was already investigated in 1-hydroxylalkyl-3-methylimidazolium based ionic liquids.¹² In addition, it is possible to synthesize required ionic liquid with tunable properties in order to obtain the most suitable solvent. For this reason, ionic liquids are so-called designed solvents. Due to their low toxicity, high conductivity and a significant electrochemical stability, ionic liquids can be used as green solvents and as a replacement for volatile organic solvents in many industrial processes.^{13,14}

In this paper, 1-(2-hydroxyethyl)-3-methylimidazolium nitrate ionic liquid was synthesized and tested as a new ionic material for cobalt(II) thermochromism. This medium contains nitrate as the anion, which is convenient because these ions form octahedral complexes with cobalt(II). Also, nitrate is the weaker ligand comparing to chloride, thus the replacement of the ligands is possible upon addition of the chloride ions. The polar hydroxyl group as the part of the ionic liquid cation provides better solubility of cobalt(II) salts. Since the complexes of cobalt(II) are coloured, the spectrophotometric method is applied to provide data on the complex structure and coordination of cobalt(II). The influence of the molecular solvent on cobalt(II) thermochromism in ionic medium was also investigated and analysed.

Although the green attributes and tunable properties of ionic liquids have helped scientist to develop many green and technologically safer processes, their impact on the environment is still under discussion.¹⁵ For new chemicals, such as ionic liquids, it is very important to evaluate their environmental impact, degradation and stability, as well as complete and safe removal from the environment. Thus, for the first time, the efficiency of different advanced oxidation processes (AOPs) for the removal of ionic liquid was investigated, including UV-induced photolysis, UV/H₂O₂ photolysis, and also heterogeneous photocatalysis by using TiO₂ Degussa P25 (hereafter Degussa P25) and TiO₂ with 7.24%, w/w Fe catalysts, in order to study its stability during the exploitation and after completing the use.

Recently, these advanced oxidation processes were applied for treating wastewater and degrading organic pollutants such as pesticides, pharmaceuticals, phenols, dyes etc.^{16–22} An attempt was also made to identify the reaction intermediates formed during the photo-oxidation process, using the LC-ESI-MS/MS and ¹H NMR techniques.

Results and Discussion

Absorption spectra

Absorption spectra of cobalt(II) in both [HO(CH₂)₂mim]NO₃ and [HO(CH₂)₂mim]NO₃·3H₂O were recorded in the absence of chloride ions at different temperatures: 298.15, 308.15, 318.15, 328.15, and 338.15 K. Spectral properties were examined in this temperature range, because it is also the range of the possible application of the thermochromic material for auto-regulated shading protection. It is clear that the overall molar absorption coefficient increase with increasing the temperature (Fig. 1) which is expected for octahedral complexes. These complexes are coloured pale pink.

In Fig. 1 the overall molar absorption coefficient ϵ defined as

$$\epsilon = A l^{-1} c_M^{-1}, \quad (1)$$

where A is the absorbance, l the light pathway and c_M the total cobalt(II) concentration, is plotted against the wavelength. Small shift of the absorption maximum towards lower energies is a consequence of cobalt(II) ligand field weakening at higher temperatures.^{4,5}

Values of the overall molar absorption coefficient in the pure ionic liquid are about ten times higher than in the system with water. This is a consequence of the water co-ordination in the coordination sphere of Co²⁺ ions. In addition, it can be seen that the position of the absorption maximum in the anhydrous system at 544 nm corresponds to the position of the absorption maxima ascribed to dodecahedral [Co(NO₃)₄]²⁻ complex species obtained in the anhydrous KNO₃-LiNO₃ eutectic melt ($\lambda_{\max} = 550$ nm)²³ and eutectic mixture 0.723CH₃CONH₂ - 0.277NH₄NO₃ ($\lambda_{\max} = 538$ nm).²⁴ In the system of [HO(CH₂)₂mim]NO₃·3H₂O an absorption maximum is shifted toward lower wavelengths (approximately at 515 nm) which corresponds to the position of the absorption maximum of octahedral cobalt(II) complexes obtained in the aqueous melt of Ca(NO₃)₂·4H₂O ($\lambda_{\max} = 512$ nm)²⁵ and diluted aqueous solutions ($\lambda_{\max} = 513$ nm).²⁶

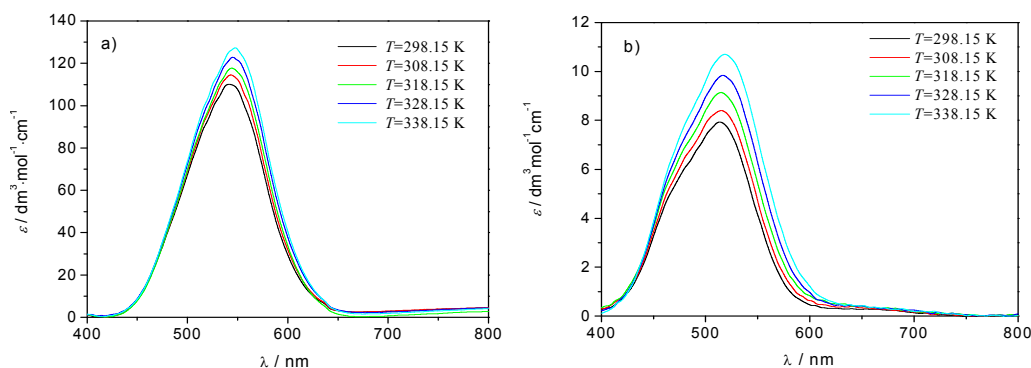


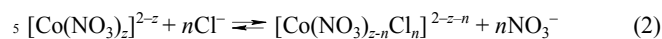
Fig. 1 Absorption spectra of cobalt(II) nitrate in: a) [HO(CH₂)₂mim]NO₃, $m(\text{Co}^{2+}) = 0.01070 \text{ mol}\cdot\text{kg}^{-1}$, and b) [HO(CH₂)₂mim]NO₃·3H₂O, $m(\text{Co}^{2+}) = 0.02960 \text{ mol}\cdot\text{kg}^{-1}$

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Addition of chloride ions to cobalt(II) nitrate solution caused a replacement of nitrate ions with chloride and formation of new absorbing species:



This change is followed by the change of colour from pale pink to dark blue (Fig. 2) and by an appearance of a new absorption band with three maxima, at 634, 669, and 696 nm in both systems.

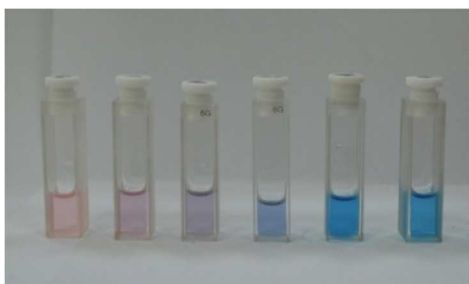


Fig. 2 Colour change of the solutions with increase of the chloride concentration

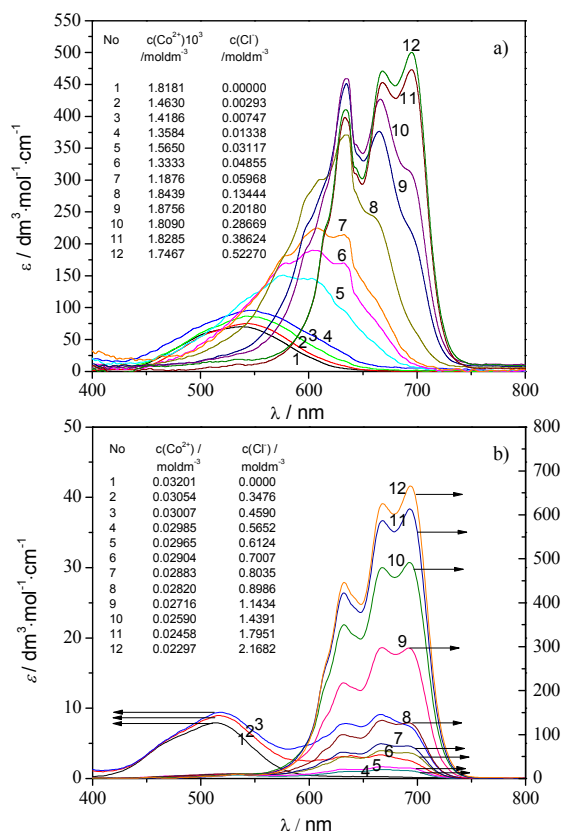


Fig. 3 Variation of cobalt(II) absorption spectra with concentration at 298.15 K in: a) pure [HO(CH₂)₂mim]NO₃, and b) [HO(CH₂)₂mim]NO₃·3H₂O

A large increase of the overall molar absorption coefficient indicate change from octahedral or dodecahedral to tetrahedral co-ordination (Fig. 3). Tetrahedral maxima occur at slightly higher wavelengths than for the cobalt(II) chloride complexes observed in concentrated aqueous HCl (625, 662, and 692 nm) ascribed to [CoCl₄]²⁻, and the aqueous melt of Ca(NO₃)₂–NH₄NO₃–H₂O (626, 662, and 690 nm).²⁷ The positions of the absorption maxima recorded in [HO(CH₂)₂mim]NO₃ have similar value to those observed in anhydrous molten KNO₃–LiNO₃ (635, 660, and 690 nm).^{4,5}

The influence of temperature on the absorption spectra of cobalt(II) in [HO(CH₂)₂mim]NO₃ is presented in Fig. 4. It can be clearly seen that there is no significant change in the intensity of the overall molar absorption coefficients with increasing the temperature, which is a consequence of the absence of thermochromic effect in pure ionic liquid. Consequently, there is no geometry change of cobalt(II) from octahedral or dodecahedral to tetrahedral in the studied ionic liquid during the heating or cooling cycles. The reasons for such behaviour (the absence of the cobalt(II) solvolysis in pure ionic liquid and thermodynamic parameters for the complexation reactions) will be discussed later.

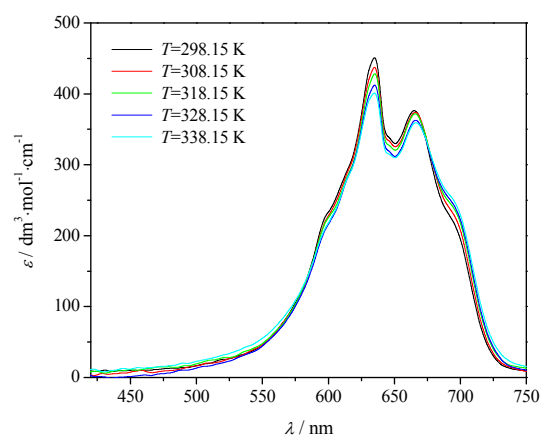


Fig. 4 Absorption spectra of cobalt(II) chloride in [HO(CH₂)₂mim]NO₃ at different temperatures; $m(\text{Co}^{2+}) = 0.001440 \text{ mol kg}^{-1}$, $m(\text{Cl}^-) = 0.15211 \text{ mol kg}^{-1}$

The quite opposite trend was found upon addition of water as molecular solvent in the ionic liquid. Here, the increase of temperature leads to a significant increase of the molar absorption coefficients, resulting in a colour change of the solutions (Fig. 5). The same observation was confirmed in our earlier study.¹¹

However, on the basis of these data it is not possible to conclude why the presence of water was necessary for the existence of thermochromic effect in the system. In order to explain it, stability constants and thermodynamic parameters were calculated on the basis of spectroscopic measurements.

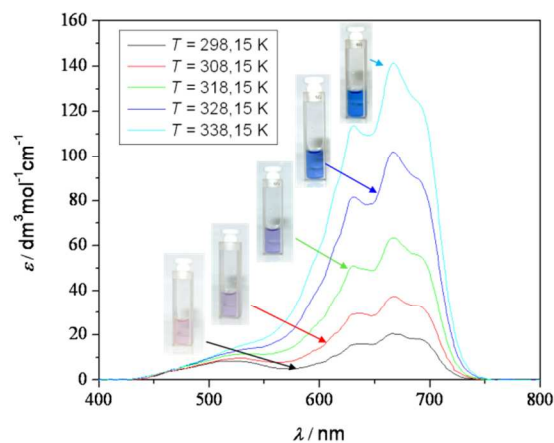


Fig. 5 Absorption spectra of cobalt(II) chloride in $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$ at different temperatures; $m(\text{Co}^{2+}) = 0.02711 \text{ mol kg}^{-1}$, $m(\text{Cl}^-) = 0.4448 \text{ mol kg}^{-1}$

5 Complex formation equilibrium

Changes in the absorption spectra upon gradual increase the chloride concentration (Fig. 3) are ascribed to complex formation. The complex formation in mixed ligand system is illustrated by a set of overall equilibrium:

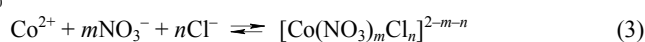


Table 1 $\log(\beta_{mn}/(\text{mol}^{-1}\text{dm}^3)^4)$ for $[\text{Co}(\text{NO}_3)_m\text{Cl}_n]^{2-m-n}$ in $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3$ and $\log(\beta_{pqr}/(\text{mol}^{-1}\text{dm}^3)^4)$ for $[\text{Co}(\text{H}_2\text{O})_p(\text{NO}_3)_q\text{Cl}_r]^{2-q-r}$ in $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$

T / K	$[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3$				$[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$			
	$[\text{Co}(\text{NO}_3)_4]^{2-}$	$[\text{Co}(\text{NO}_3)_3\text{Cl}]^{2-}$	$[\text{Co}(\text{NO}_3)_2\text{Cl}_2]^{2-}$	$[\text{Co}(\text{NO}_3)\text{Cl}_3]^{2-}$	$[\text{CoCl}_4]^{2-}$	$[\text{Co}(\text{H}_2\text{O})_2(\text{NO}_3)_4]^{2-}$	$[\text{Co}(\text{H}_2\text{O})_2(\text{NO}_3)_2\text{Cl}_2]^{2-}$	$[\text{CoCl}_4]^{2-}$
298.15	2.79 ± 0.05	4.85 ± 0.07	5.70 ± 0.05	7.98 ± 0.20	9.86 ± 0.10	1.09 ± 0.04	1.39 ± 0.08	3.09 ± 0.04
308.15	2.76 ± 0.05	4.70 ± 0.03	5.77 ± 0.21	7.76 ± 0.05	9.61 ± 0.05	1.80 ± 0.03	2.14 ± 0.06	4.00 ± 0.02
318.15	2.69 ± 0.03	4.67 ± 0.02	5.61 ± 0.18	7.55 ± 0.04	9.36 ± 0.02	2.40 ± 0.03	2.79 ± 0.05	4.79 ± 0.02
328.15	2.62 ± 0.05	4.65 ± 0.07	5.45 ± 0.07	7.38 ± 0.09	9.13 ± 0.03	3.10 ± 0.03	3.65 ± 0.05	5.70 ± 0.02
338.15	2.58 ± 0.07	4.62 ± 0.06	5.23 ± 0.10	7.25 ± 0.03	8.95 ± 0.08	3.81 ± 0.03	4.59 ± 0.03	6.58 ± 0.02

As seen from Table 1, the values of the stability constants in $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3$ for each complex slightly decrease with temperature, which is not usual behaviour of the cobalt(II) complexes investigated earlier in nitrate melts.^{11,27,31} In the case of $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$, the stability constants increase with temperature as expected.

50 Thermodynamic parameters

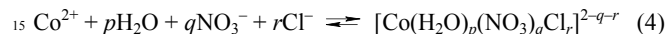
Using the constants from Table 1, the standard thermodynamic functions for the complex formation in $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3$ and $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$ were calculated. The standard enthalpy and entropy changes ΔH° and ΔS° have been

estimated from the temperature variation of

$$\Delta G^\circ = -RT \ln \beta \quad (7)$$

The thermodynamic parameters have been calculated from the

in the pure ionic liquid, and in the mixture with water:



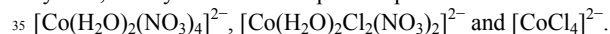
The overall stability constants are expressed as:

$$\beta_{mn} = [\text{Co}(\text{NO}_3)_m\text{Cl}_n]^{2-m-n} / [\text{Co}^{2+}][\text{NO}_3^-]^m[\text{Cl}^-]^n \quad (5)$$

$$20 \beta_{pqr} = [\text{Co}(\text{H}_2\text{O})_p(\text{NO}_3)_q\text{Cl}_r]^{2-q-r} / [\text{Co}^{2+}][\text{H}_2\text{O}]^p[\text{NO}_3^-]^q[\text{Cl}^-]^r \quad (6)$$

On the basis of the cobalt(II) co-ordination by halide ions in other solvents, we assumed that the complexes were mononuclear. For the computation of stability constants the nonlinear least-squares programs STAR²⁸ and HypSpec^{29,30} were utilized.

The part of these programs is used to determine the number of absorbing species in a chosen wavelength range by factor analysis. From a large number of trials, it was concluded that the following complexes were formed in the case of pure ionic liquid solution: $[\text{Co}(\text{NO}_3)_4]^{2-}$, $[\text{Co}(\text{NO}_3)_3\text{Cl}]^{2-}$, $[\text{Co}(\text{NO}_3)_2\text{Cl}_2]^{2-}$, $[\text{Co}(\text{NO}_3)\text{Cl}_3]^{2-}$ and $[\text{CoCl}_4]^{2-}$. In the $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$ system, only three complex species were determined:



The stability constants of these complexes were calculated, together with the molar absorption coefficients of the complexes at each relevant wavelength. The average values of the stability constants calculated by both programs are given in Table 1.

formation constants expressed in the molarity scale and obtained values are presented in Table 2. For conversion of all concentrations expressed as $\text{mol} \cdot \text{kg}^{-1}$, density of the investigated solutions was required at different temperatures. The density results are summarized in the Experimental part of the manuscript.

It was found that the formation of all complexes is exothermic process in $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3$. It is well-known that the octahedral-tetrahedral transformation of cobalt(II) is strongly favoured by an increase of temperature or halide concentration or both.²⁶ Unfortunately, the thermodynamic calculations suggest that octahedral complexes cannot be converted into tetrahedral species in pure ionic liquid. The replacement of the nitrate by the chloride ions is not favoured, since the entropy change is neglected (the total number of species in the system remains the same after complexation). Thus, thermochromism of cobalt(II) in synthesized ionic liquid was not observed.

Complex formation in aqueous $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$

system was found to be endothermic with prominent entropy change due to an increasing number of species in the reactions. This can be explained by the presence of the water molecules in the co-ordination sphere of dodecahedral cobalt(II) complexes.

Since the obtained absorption spectra of tetrahedral $[\text{CoCl}_4]^{2-}$ in $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$ corresponds to spectra in anhydrous melts, presence of the water molecules in this complex is excluded. Thus, complex formation equilibria in $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$ can be described by the following equation:



From all of these observations, it can be concluded that for the existence of cobalt(II) thermochromism in ionic media, the crucial is the presence of small amount of molecular liquid (such as water) which will increase the standard entropy of the complexation reaction and change of the geometry of cobalt(II) from octahedral to tetrahedral.

Table 2 Standard enthalpy and entropy values for cobalt(II) chloride complex formation in the temperature range from 298.15 to 338.15 K in $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3$ and $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$

	$[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3$				$[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$			
	$[\text{Co}(\text{NO}_3)_4]^{2-}$	$[\text{Co}(\text{NO}_3)_3\text{Cl}]^{2-}$	$[\text{Co}(\text{NO}_3)_2\text{Cl}_2]^{2-}$	$[\text{Co}(\text{NO}_3)\text{Cl}_3]^{2-}$	$[\text{CoCl}_4]^{2-}$	$[\text{Co}(\text{H}_2\text{O})_2(\text{NO}_3)_4]^{2-}$	$[\text{Co}(\text{H}_2\text{O})_2(\text{NO}_3)_2\text{Cl}_2]^{2-}$	$[\text{CoCl}_4]^{2-}$
$\Delta H^\circ / \text{kJ mol}^{-1}$	-10.9 ± 0.9	-9.8 ± 2.5	-24.6 ± 6.4	-35.4 ± 1.3	-44.5 ± 0.8	130.2 ± 4.2	153.6 ± 9.2	167.7 ± 4.5
$\Delta S^\circ / \text{J mol}^{-1}\text{K}^{-1}$	17 ± 3	59 ± 8	29 ± 10	34 ± 4	40 ± 2	457 ± 13	540 ± 29	621 ± 14

Using the stability constants from Table 1, it was also possible to calculate resolved species spectra of each complex in both, pure ionic liquid (Fig. 6a) and ionic liquid + water mixture (Fig. 6b). As it can be seen from Fig. 6, resolved spectra for the dodecahedral complexes formed in the absence of chloride ions

(ϵ_{40} for $[\text{Co}(\text{NO}_3)_4]^{2-}$ in $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3$ and ϵ_{402} for $[\text{Co}(\text{H}_2\text{O})_2(\text{NO}_3)_4]^{2-}$ in $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$) are in the excellent agreement with the experimental spectra obtained in the solutions without chloride ions (Fig. 1). This also suggests that the calculations, models and conclusions mentioned above in the manuscript are valid and reliable.

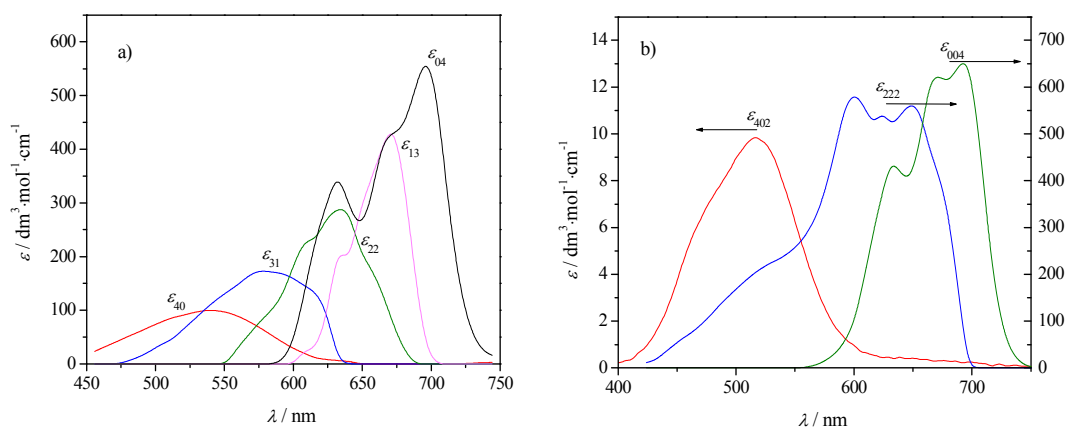


Fig. 6 Resolved species spectra of cobalt(II) complexes in a) $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3$ and b) in $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$ at 328.15 K

The resolved species spectra in pure ionic liquid and $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$ obtained for $[\text{CoCl}_4]^{2-}$ (ϵ_{04} and ϵ_{004}) corresponds to tetrahedral co-ordination of cobalt(II) with the characteristic shape of the absorption band, absorption maxima positions and high ϵ values.

This spectra agrees excellently with those reported for tetrahedral $[\text{CoCl}_4]^{2-}$ in solid Cs_2CoCl_4 ,³² 12 mol dm^{-3} aqueous HCl ,³³ pyridine hydrochloride,³⁴ and molten alkali chlorides such as eutectic $\text{KCl}-\text{AlCl}_3$ ³⁵ or CsCl .³⁶

The resolved spectrum of mixed chloride – nitrate complex in $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$ (described in the Fig. 6b with ϵ_{222} overall molar absorption coefficient) is showed the most pronounced change with the increase of the temperature as

presented in Fig. 7. It can be concluded that formation of mixed complex $[\text{Co}(\text{H}_2\text{O})_2(\text{NO}_3)_2\text{Cl}_2]^{2-}$ is the most responsible for thermochromism of cobalt(II) in ionic liquid + water mixture.

Effects of type of AOPs

Ionic liquid $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3$ strongly absorbs UV irradiation over a range of wavelengths, from 200 to 240 nm (Fig. 8), with the maximum absorption band at 210 nm. Hence, only those UV sources with good output below 240 nm can be used for direct photolysis of $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3$. Since the radiation of high-pressure mercury lamp below of closely 275 nm can not pass through Pyrex glass, no direct photolysis of $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3$ could be expected. To investigate the direct photolysis of $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3$, the first experiments were performed with

[HO(CH₂)₂mim]NO₃ dissolved in distilled water and at natural pH of 5.0. After 240 min of irradiation, no significant change in the [HO(CH₂)₂mim]NO₃ concentration could be observed (Fig. 9), which is in agreement with the above discussion.

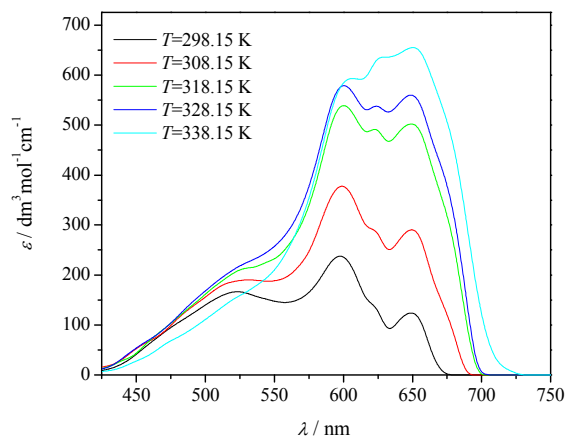


Fig. 7 Resolved species spectra of [Co(H₂O)₂(NO₃)₂Cl₂]²⁻ in [HO(CH₂)₂mim]NO₃·3H₂O at different temperatures

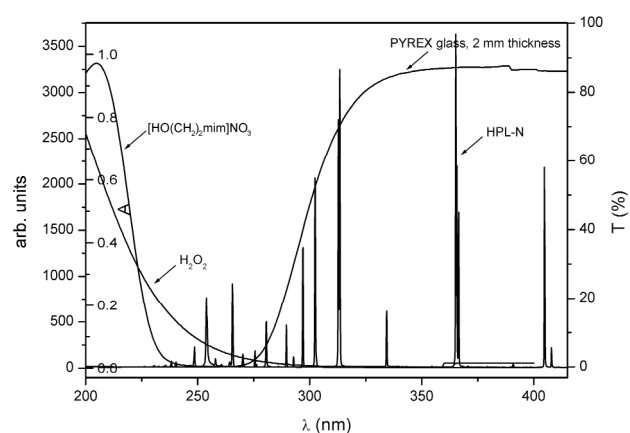


Fig. 8 UV emission spectra of HPL-N lamp (left axis, out scale) and molar absorption spectrum of [HO(CH₂)₂mim]NO₃ ($c_0 = 3.8 \cdot 10^{-2}$ mM) and H₂O₂ (45.3 mM) (left axis, in scale) and Pyrex glass (right axis)

From Fig. 9 (inset) it can be deduced that the decomposition rate in all cases seems to follow a pseudo-first order reaction, and therefore a plot of $\ln(c/c_0)$ versus time should give a straight line (the inset of Fig. 9). The rate constants, k , were obtained from least-squares linear regression analysis, all with correlation coefficients greater than 0.98.

Fig. 9 illustrates the efficiency of different AOPs for the degradation of [HO(CH₂)₂mim]NO₃. Besides the result of [HO(CH₂)₂mim]NO₃ degradation by direct photolysis, it shows the results of photochemical tests obtained using Degussa P25, H₂O₂, as well as 7.2Fe/TiO₂/H₂O₂ system. In experiments with H₂O₂, because of its depletion, H₂O₂ was added successively (70 μ l each hour during the irradiation).

The investigation of the effect of the presence of H₂O₂ showed that indirect photolysis in the presence of H₂O₂ (Table 3) was much more efficient than direct photolysis. These findings

indicated that [HO(CH₂)₂mim]NO₃ decomposition is enhanced greatly compared to the direct photolysis due to the production of [•]OH in UV/H₂O₂ process. In addition to this photodecomposition by using Degussa P25 was most efficient, and the complete removal of [HO(CH₂)₂mim]NO₃ required only 240 min. Reduced efficiency of indirect photolysis compared to photocatalytic with Degussa P25 can be explained by the fact that only radiation with wavelengths less than 300 nm can cause photolysis of hydrogen peroxide.³⁷ Fig. 8 shows that a relatively small amount of this radiation passes through a Pyrex glass. On the other hand, from the absorption spectrum of Degussa P25³⁷ it can be concluded that all radiation that passes through the Pyrex glass was used, which leads to increased efficiency of degradation.

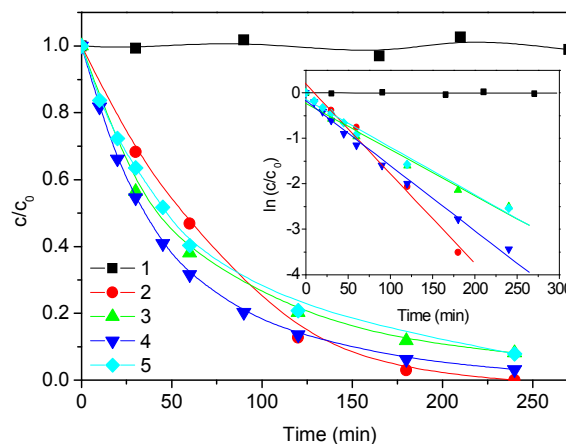


Fig. 9 Degradation kinetics of [HO(CH₂)₂mim]NO₃ ($c_0 = 0.38$ mM) by using different procedures: (1) direct photolysis; (2) Degussa P25 (1.67 g l⁻¹); (3) 45 mM H₂O₂ + 70 μ l h⁻¹ H₂O₂; (4) 7.2Fe/TiO₂ (1.67g l⁻¹) + 45 mM H₂O₂ + 70 μ l h⁻¹ H₂O₂ at pH 2.80; (5) 7.2Fe/TiO₂ (1.67g l⁻¹) + 45 mM H₂O₂ + 70 μ l h⁻¹ H₂O₂ at pH 5.0. The inset shown pseudo-first-order kinetics plots

7.2Fe/TiO₂/H₂O₂ system was used to study the efficiency of heterogeneous photo-Fenton oxidation. For this system photodegradation experiments were conducted at pH 5.0 and 2.8,¹⁷ and as can be seen from Table 3 this change removal efficiency for only 4.7%.

Table 3 Rate constants of [HO(CH₂)₂mim]NO₃ degradation by UV, UV/TiO₂, UV/H₂O₂, UV/7.2Fe/TiO₂/H₂O₂ processes ($c_0 = 0.38$ mM)

Process	Initial pH	Rate constant, ($k \times 10^2$) / min ⁻¹	Removal ^a / %
Photolysis	5.0	—	—
Degussa P25	5.0	1.98	100
45 mM H ₂ O ₂ + 70 μ l h ⁻¹ H ₂ O ₂	5.0	1.02	91.8
7.2Fe/TiO ₂ + 45 mM H ₂ O ₂ + 70 μ l h ⁻¹ H ₂ O ₂	5.0	1.05	92.1
7.2Fe/TiO ₂ + 45 mM H ₂ O ₂ + 70 μ l h ⁻¹ H ₂ O ₂	2.8	1.43	96.8

^a Removal percentage at 240 min.

As can be seen from the Table 3, the degradation efficiencies of [HO(CH₂)₂mim]NO₃ by four processes tested by the sequence were UV < UV/H₂O₂ < UV/7.2Fe/TiO₂/H₂O₂ < UV/TiO₂. It should be noted that for the last three photochemical process efficiency of degradation after 240 min varies for only 8%, and

from the standpoint of environmental protection, cost of chemicals and in conjunction with artificial sources of radiation the most applicable would be UV/H₂O₂ process.

Intermediates of photodegradation

5 Identification of the intermediates was also carried out by analysis ¹H NMR (Fig. 10). The standard proton spectrum recorded for [HO(CH₂)₂mim]NO₃ in D₂O before irradiation contained following significant signals [δ_{H} (ppm)]: [8.72 (*s*, 1H, H-2), 7.45 (*d*, 2H, *J*_{4,5} = 14 Hz, H-4 and H-5), 4.28 (*m*, 2H, 10 OCH₂), 3.89 (*m*, 2H, NCH₂), 3.87 (*s*, 3H, NCH₃)].

After 120 minutes of photodegradation in the NMR spectrum three new signals were identified, at 2.99, 2.73 and 2.56 ppm. The intensities of these signals were increased as degradation of the starting [HO(CH₂)₂mim]NO₃ moiety progressed. Also, after the same time of degradation in the NMR spectrum a signal was observed at 8.92 ppm which originates from the changed aromatic structure. Signal intensity of this intermediate (8.92 ppm) showed slower increase during photodegradation. During the entire period of photodegradation, in aromatic region the existence of another intermediate was observed (signal at 8.87 ppm) with very low actual concentration. In addition, after 240 minutes of degradation the new signal was observed at 3.77 ppm. In the following next five hours of degradation intensity of this signal was increased, and then decreased up to the end of 25 experiment.

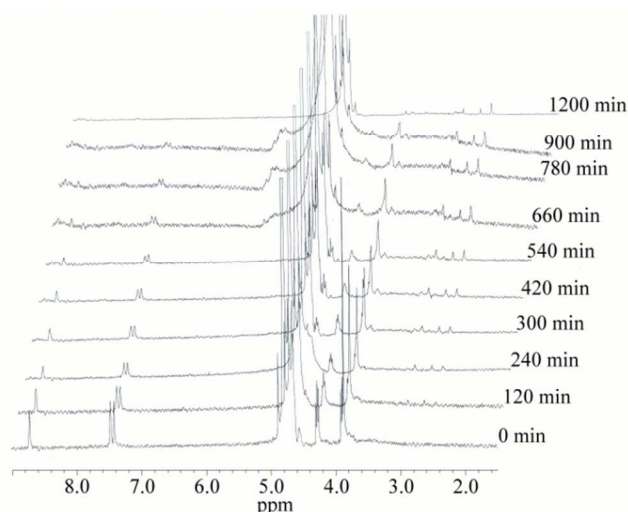


Fig. 10 Temporal ¹H NMR spectral profiles during the photodecomposition of [HO(CH₂)₂mim]NO₃ in D₂O solution (*c*₀ = 3.8 mM) in the presence of Degussa P25 (1.67 g l⁻¹)

30 The existence of *N*-methylformamide (**P3**) at Fig. 11, as intermediate formed during the photocatalytic degradation was confirmed by adding an authentic internal standard of *N*-methylformamide and overlapping its signals of with those obtained during the photodegradation [δ_{H} (ppm)]: [2.71 (*s*, NCH₃), 7.97 (*s*, COH)]. Based on the kinetic curves and the corresponding absorption spectra of intermediates obtained from HPLC–DAD method, the existence of this intermediate is also established in the experiment of indirect photolysis (Fig. 9). The LC–ESI–MS/MS technique identified [HO(CH₂)₂mim]NO₃ (**1**) and **P2** (Fig. 11) based on their MS/MS fragmentation data (Table 4).

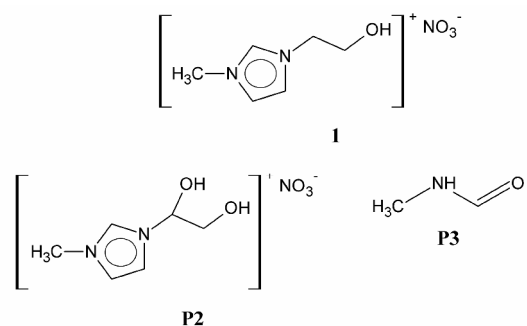


Fig. 11 Structure of the studied [HO(CH₂)₂mim]NO₃ (**1**) and proposed structures for photodegradation products (**P2**) and (**P3**) in the presence of Degussa P25

Table 4 MS/MS fragmentation data for [HO(CH₂)₂mim]NO₃ (**1**) and its intermediate obtained in positive mode.

Peak label	<i>M</i> _{mi} / g mol ⁻¹	Precursor ion <i>m/z</i>	<i>V</i> _{col} / V	Product ions <i>m/z</i> (relative abundance)
1	126	127	0	127 (100)
			10	127 (100), 83 (58)
			20	127 (11), 83 (100)
			30	95 (6), 83 (100), 56 (16)
P2	142	143	0	143 (100), 125 (14)
			10	143 (30), 125 (100), 97 (7)
			20	125 (100), 97 (43), 96 (34), 95 (26), 83 (11), 56 (12)
			30	125 (13), 97 (22), 96 (52), 95 (100), 83 (13), 56 (20)

P2 (likely 1-(1,2-dihydroxyethyl)-3-methylimidazolium nitrate) represents a compound with *M*_{mi} = 142, which is by 16 units higher than the molecular mass of [HO(CH₂)₂mim]NO₃ and that indicates the addition of the hydroxyl group. Intermediate **P2** fragmentation starts with water loss ($\Delta m/z = 18$) from secondary alcohol. Formed enol isomerizes into aldehyde, that loses CO ($\Delta m/z = 28$) yielding 1,3-dimethylimidazolium cation. Parallel reaction is formation of methylimidazolium cation (*m/z* = 83) by loss of ketene ($\Delta m/z = 42$) from aldehyde. Final fragmentation product, methylaziranium ion (*m/z* = 56) is formed by HCN loss ($\Delta m/z = 27$) accompanied by ring contraction.

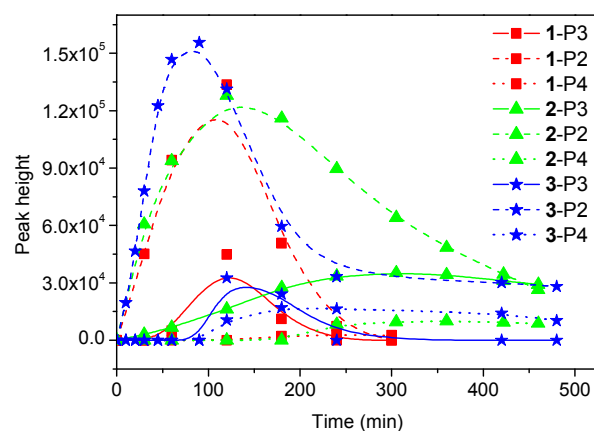


Fig. 12 Kinetics of intermediate formation during photodegradation of [HO(CH₂)₂mim]NO₃ (*c*₀ = 0.38 mM) by different AOPs: (**1**) Degussa P25 (1.67 g l⁻¹); (**2**) 45 mM H₂O₂ + 70 µl h⁻¹ H₂O₂; (**3**) 7.2Fe/TiO₂ (1.67g l⁻¹) + 45 mM H₂O₂ + 70 µl h⁻¹ H₂O₂ at pH 2.80

Based on the obtained data (Fig. 12) it can be concluded that the induced photolytic with H_2O_2 and photocatalytic degradation conducted by the same reaction mechanism. Methods used cannot determine the structure of **P4**, but it is supposed that the magnification nonpolarity (HPLC–DAD results) was probably due to oxidation of hydroxyl groups of **P2** and introducing carbonyl group.

Experimental part

Chemicals and solutions

All used chemicals were pro analysis products. For the synthesis of ionic liquid, 2-chloro-1-ethanol (Fluka), *N*-methylimidazole (Sigma-Aldrich), ethyl acetate (Backer) and silver nitrate (Poch) were used.

The synthetic path of 1-(2-hydroxyethyl)-3-methylimidazolium nitrate is presented in Fig. 13. A 250 cm^3 three-neck round-bottom flask was filled with 2-chloro-1-ethanol (88 cm^3 , 1.30 mol), freshly distilled *N*-methylimidazole (94 cm^3 , 1.17 mol) and 50 cm^3 of ethyl acetate. The mixture was stirred and heated under the reflux for one week at 352 K. Yellow crystals were obtained after the cooling. The solid was re-crystallized from dry ethanol four times. The purity of the obtained white crystals was checked by potentiometric titration of the chloride ions ($\omega(\text{Cl}) = 0.9801$). Then, a calculated amount of the crystals (69.2 g, 0.4259 mol) was mixed with AgNO_3 (74.0 g, 0.4354 mol) and 60 cm^3 of water. The mixture was stirred in the round-bottom flask for 120 minutes. The resulting white precipitate (silver chloride) was removed and the obtained liquid is purified using activated charcoal. A clear colourless liquid was obtained. A yield of the product was 95%. (The amount of silver and chloride ions in the product was determined by potentiometric titration.). In order to remove water and other volatile organic compounds from the sample, the ionic liquid was heated for 72 h at 323.15 K under vacuum. Then, it was conditioned under a nitrogen atmosphere, which was selected because of its low solubility in the investigated ionic liquids. After drying, the water content in IL was found to be less than 10^{-4} %.

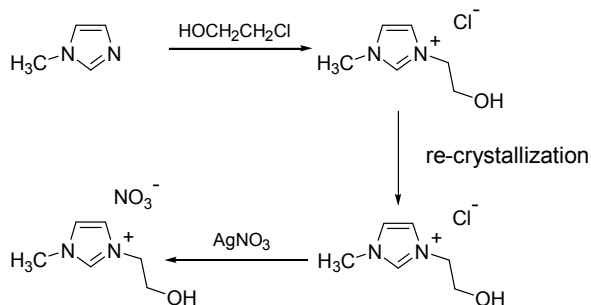


Fig. 13 Synthetic path of 1-(2-hydroxyethyl)-3-methylimidazolium nitrate

The ^{13}C and ^1H NMR spectra of ionic liquid were recorded on a Bruker AC-250 spectrometer. ^1H NMR (D_2O): δ 3.92 (*s*, 3 H); 3.92 (*t*, 2 H); 4.41 (*t*, 2 H, $J = 4.8$ Hz); 7.55 and 7.60 (2*xs*, 2 H); 8.85 (*s*, 1 H). ^{13}C NMR (D_2O): δ 38.12 (*q*, CH_3); 54.09 (*t*, $\text{CH}_2\text{CH}_2\text{OH}$); 62.36 (*t*, $\text{CH}_2\text{CH}_2\text{OH}$); 124.92 and 126.02 (2*xdd*, C-4 and C-5); 139.04 (*d*, C-2). Two resonant structures of investigated ionic liquid are presented in Fig. 14.

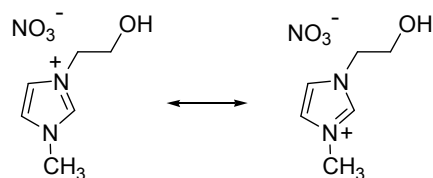


Fig. 14 The resonant structures of 1-(2-hydroxyethyl)-3-methylimidazolium nitrate

50

For additional characterization, the IR spectra of ionic liquids were recorded. The observed peak at 1344 cm^{-1} indicates the presence of nitrate ions, while the peak appeared at 3394 cm^{-1} indicates existence of hydroxyl group in the ionic liquid.

Density

The vibrating tube densimeter, Rudolph Research Analytical DDM 2911, was used for density measurements. The accuracy and precision of the densimeter were $\pm 0.00001\text{ g cm}^{-3}$. The instrument was automatically thermostated (Peltier-type) within $\pm 0.02\text{ K}$ and was calibrated at the atmospheric pressure before each series of measurements. The calibration was performed using ambient air and bidistilled ultra pure water. The density of the samples was measured in the temperature range from 283.15 K up to 353.15 K at different chloride concentration. The density dependence on temperature (T in K) and chloride concentration (m in $\text{mol}\cdot\text{kg}^{-1}$) was a linear function and may be summarized by the following relation:

$$d = 1,35371 - 8,297 \cdot 10^{-4}T + (0,00625 + 4,58 \cdot 10^{-5}T)m(\text{Cl}^-) \quad (9)$$

Vis-spectroscopy

The stock solution of cobalt(II) nitrate in ionic liquid was prepared by measuring the appropriate amounts of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3$. The solution was heated to remove the water from the system, which has been previously added as cobalt(II) nitrate hexahydrate. The series of 11 solutions with different cobalt(II)/chloride ratios (from 2 to 300) in pure ionic liquid were prepared for the spectrophotometric measurements. For the measurements of the cobalt(II) absorption spectra in $[\text{HO}(\text{CH}_2)_2\text{mim}]\text{NO}_3 \cdot 3\text{H}_2\text{O}$, the appropriate amounts of ionic liquid, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and water were measured. The series of 14 solutions with different cobalt(II)/chloride ratios (from 0 to 95) in this solvent were prepared and recorded spectrophotometrically.

The absorption spectra of the solutions with variable chloride and cobalt(II) concentration were recorded in the wavelength range 400–800 nm on a Secomam Anthelie Advanced 2 spectrophotometer with thermostated cell compartments at 298.15, 308.15, 318.15, 328.15 and 338.15 K. The temperature was kept constant to $\pm 0.1\text{ K}$.

Photostability of 1-(2-hydroxyethyl)-3-methylimidazolium nitrate

The concentration of the 1-(2-hydroxyethyl)-3-methylimidazolium nitrate stock solution used in photodegradation experiments was 0.38 mM and 3.8 mM. 30% H_2O_2 , 99.8% acetonitrile (ACN, HPLC gradient grade), and 99% *N*-methylformamide were purchased from Sigma-Aldrich; 85%

H₃PO₄ was a product Lachema (Neratovice, Czech Republic); NaOH was a product of Zorka Pharm (Šabac, Serbia), and H₂SO₄ was purchased from Merck. All solutions were made using doubly distilled water, except for the ¹H NMR measurements where 99.9% D₂O purchased from Sigma-Aldrich was used as solvent.

Fe/TiO₂ with 7.24% of Fe (w/w, denoted as 7.2Fe/TiO₂)¹⁵ and Degussa P25 (75% anatase and 25% rutile form, surface area of 50 m² g⁻¹, and average particle size about 20 nm, according to the producer's specification), were used as photocatalysts.

Photodegradation procedure

A typical photocatalytic experiment was carried out in a batch reactor made of Pyrex glass (total volume of cca 100 cm³, solution depth 46 mm). A Philips HPL-N 125 W high-pressure mercury lamp ($\lambda > 290$ nm) was used as the UV source. It has emission bands in the UV region at 304, 314, 335 and 366 nm, with the maximum emission at 366 nm. The radiation intensity was 3.57 mW cm⁻².

The experiments were carried out using 30 cm³ of solution of [HO(CH₂)₂mim]NO₃ containing 1.67 g l⁻¹ of catalyst and/or 45 mM H₂O₂ with successive addition of H₂O₂ (70 μ l each hour during the radiation) (except for the study of direct photolysis). In the case with Degussa P25 as catalyst H₂O₂ was absent. All experiments were performed at the natural pH (~ 5.0), except when studying the influence of the pH on 7.2 Fe/TiO₂ catalyst. pH was adjusted by adding solution of H₂SO₄ or NaOH. The suspension was stirred continuously in dark for 15 min prior to turning on the UV lamp as to ensure equilibrium adsorption of [HO(CH₂)₂mim]NO₃ on the photocatalyst. Oxygen (99.99% purity) was continuously fed to the bottom of the reactor at a constant flow rate of 5 cm³ min⁻¹. Apart from oxygen bubbling the solution was homogenized with the aid of a stirring bar, to ensure completely mixed batch conditions. The control experiments carried out under O₂ flow by stopping the irradiation showed that there were no losses of volatile compounds during the degradation. The temperature of the reaction solution was maintained at 298 \pm 0.5 K throughout the experiment using a water circulation system.

Analytical procedure

For the kinetic studies of [HO(CH₂)₂mim]NO₃ (0.38 mM) removal and its photodegradation intermediates by liquid chromatography–diode array detection (HPLC–DAD), 0.5 cm³ aliquots of the reaction mixture were sampled at the beginning of the experiment and at various time intervals, followed by filtration through Millipore (Millex-GV, 0.22 μ m) membrane filter (in the presence of photocatalyst). The absence of adsorption of ionic liquid onto the filters was confirmed by a preliminary test. A Shimadzu UFLC liquid chromatograph equipped with UV–vis diode array detection and a Zorbax Eclipse XDB-C18 (150 mm \times 4.6 mm i.d., particle size 5 μ m) column were used. The injection volume was 20 μ l. Column temperature was held at 298.15 K, the eluent was a mixed solution of 0.1% H₃PO₄–ACN (6:4, v/v), pH 2.56, and the total flow rate was 0.8 cm³ min⁻¹. The ionic liquid elution was monitored at 210 nm (absorption maximum for ionic liquid), the retention time being 1.54 min.

Absorbance spectra were recorded on a double-beam T80+

UV-vis Spectrometer (UK), at a fixed slit width (2 nm), using 1 cm quartz cell and computer-loaded UV Win 5 data software. The UV energy flux was measured using a Delta Ohm HD 2102.2 (Padova, Italy) radiometer that was fitted with the LP 471 UVA sensor (spectral range 315–400 nm).

The ¹H NMR spectra of [HO(CH₂)₂mim]NO₃/D₂O solution (3.8 mM, sample volume 1.0 cm³) during illumination in the presence of Degussa P25 particles were recorded on a Bruker AC-250 spectrometer. Filtration was carried out to separate the TiO₂ particles as previously described. Experimental conditions: temperature of samples 296 K, data points 16 K, time domain 16 K, receiver gain 10, pulse width 3.0 μ s, acquisition time 2.736 s, spectral width 3000 Hz, and line broadening 0.2. The numbers of scans was 265.

For the LC–ESI–MS/MS evaluation of intermediates (3.8 mM) of [HO(CH₂)₂mim]NO₃ was prepared. Filtration was carried out to separate the Degussa P25 particles as previously described. Then, a 20 μ l sample was injected and analyzed on an Agilent Technologies 1200 series LC with Agilent Technologies 6410A series electrospray ionization triple-quadrupole MS/MS, using Agilent Technologies Zorbax XDB-C18 column (50 mm \times 4.6 mm i.d., particle size 1.8 μ m, 313 K). The mobile phase (flow rate 1 cm³ min⁻¹) consisted of 0.1% aqueous formic acid and ACN (gradient: 0 min 30% ACN, 1.5 min 40.5%, post time 0.5 min). Analytes were ionized using the electrospray ion source, with nitrogen as drying gas (temperature 623 K, flow 10 dm³ min⁻¹) and nebulizer gas (45310.26 kPa), and a capillary voltage of 4.0 kV. High-purity nitrogen was used as the collision gas. Full scan mode (m/z range 50–500, scan time 100 ms, fragmentor voltage 100 V), using both polarities, was adopted to examine isotopic peaks distribution and obtain structural information. To identify the detected compounds, product ion scan analysis (MS² experiment) was used, with [M+H]⁺ ions as precursors, and collision energies in 10–30 V interval (10 V increments).

Conclusions

Ionic liquid 1-(2-hydroxyethyl)-3-methylimidazolium nitrate was synthesized in this work. The structure was confirmed by both ¹H NMR and IR spectroscopy. The density of this liquid was measured in the temperature range from 283.15 K to 353.15 K. The spectrophotometric measurements of cobalt(II) nitrate and cobalt(II) chloride series solutions in [HO(CH₂)₂mim]NO₃ and [HO(CH₂)₂mim]NO₃·3H₂O at 298.15, 308.15, 318.15, 328.15, and 338.15 K were performed. According to the spectrophotometric measurements and calculations of the stability constants and thermodynamic parameters, it was concluded that pure ionic liquid due to the absence of cobalt(II) solvolysis and unfavourable entropy values for the complexation reaction, could not be used as a suitable medium for cobalt(II) thermochromism. Addition of small amount of molecular solvent (water) increases the entropy of the system and pronounce thermochromism of cobalt(II) in ionic liquid + water mixture. Also, photostability of [HO(CH₂)₂mim]NO₃ was examined for the first time by applying four different AOPs: UV, UV/H₂O₂, UV/7.2Fe/TiO₂/H₂O₂ and UV/TiO₂ Degussa P25. It was observed that indirect photolysis in the presence of H₂O₂ was much more efficient than direct photolysis. By applying photocatalyst Degussa P25 and 7.2Fe/TiO₂/H₂O₂ after 240 minutes of UV irradiation, complete

decomposition of ionic liquids was achieved. For 7.2Fe/TiO₂/H₂O₂ system change in pH values from 5.0 to 2.8 had no effect on the efficiency of [HO(CH₂)₂mim]NO₃ degradation. It was also found that the decomposition rate of [HO(CH₂)₂mim]NO₃ for all applied AOPs was followed a pseudo-first-order reaction. For studied AOPs the same degradation products were found, which points to the same mechanism of degradation.

Acknowledgement

This work was financially supported by the Ministry of Education, Science and Technological Development of Republic of Serbia under project contracts ON172012, ON172042 and The Provincial Secretariat for Science and Technological Development of APV.

Notes and references

* Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, University of Novi Sad, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia.
Fax: +381 21 454065; Tel: +381 21 4852744;

E-mail: slobodan.gadzuric@dh.uns.ac.rs

- 1 M. Santamouris, C. A. Balaras, E. Descalaki, M. Vallindras, *Solar Energy*, 1994, **53**, 411.
- 2 P. Pan, N. J. Susak, *Geochim. Cosmochim. Acta*, 1989, **53**, 327.
- 3 L. H. Skibsted, J. Bjerrum, *Acta Chem. Scand.*, 1978, **32**, 429.
- 4 I. V. Tananaev, R. F. Dzurinskii, *Dokl. Akad. Nauk SSSR*, 1960, **134**, 1374.
- 5 I. V. Tananaev, R. F. Dzurinskii, *Dokl. Akad. Nauk SSSR*, 1960, **135**, 1394.
- 6 D. H. Kerridge, R. Nikolić, D. Stojić, *J. Chem. Soc. Dalton Trans.*, 1986, 1663.
- 7 J. Savović, R. Nikolić, D. Veselinović, *J. Sol. Chem.*, 2004, **33**, 287.
- 8 B. Matijević, I. Zsigrai, M. Vraneš, S. Gadžurić, *J. Mol. Liq.*, 2010, **154**, 82.
- 9 M. Vraneš, S. Gadžurić, S. Dožić, I. Zsigrai, *J. Chem. Eng. Data*, 2010, **55**, 2000.
- 10 M. Vraneš, S. Gadžurić, I. Zsigrai, S. Dožić, *J. Mol. Liq.*, 2010, **152**, 34.
- 11 S. Gadžurić, M. Vraneš, S. Dožić, *Sol. Energy Mater. & Sol. Cells*, 2012, **105**, 309.
- 12 X. Wei, L. Yu, D. Wang, X. Jin, G. Z. Chen, *Green Chem.*, 2008, **10**, 296.
- 13 M. Koel, *Ionic Liquids in Chemical Analysis*, Taylor & Francis Group, CRC, New York, 2009.
- 14 A. Berthod, B. S. Carda, *Anal. Bioanal. Chem.*, 2004, **380**, 168.
- 15 D. Adam, *Nature*, 2000, **407**, 938.
- 16 B. F. Abramović, N. D. Banić, D. V. Šojić, *Chemosphere*, 2010, **81**, 114.
- 17 N. Banić, B. Abramović, J. Krstić, D. Šojić, D. Lončarević, Z. Cherkazova-Zheleva, V. Guzsány, *Appl. Catal. B: Environ.*, 2011, **107**, 363.
- 18 D. Šojić, V. Despotović, D. Orčić, E. Szabó, E. Arany, S. Armaković, E. Illés, K. Gajda-Schranz, A. Dombi, T. Alapi, E. Sajben-Nagy, A. Palágyi, Cs. Vágvolgyi, L. Manczinger, L. Bjelica, B. Abramović, *J. Hydrol.*, 2012, **472-473C**, 314.
- 19 S. Ahmed, M. G. Rasul, W. N. Martens, R. Brown, M. A. Hashib, *Desalination*, 2010, **261**, 3.
- 20 A. Y. C. Tong, R. Braund, D. S. Warren, B. M. Peake, *Cent. Eur. J. Chem.*, 2012, **10**, 989.
- 21 M. Pera-Titus, V. García-Molina, M. A. Baños, J. Giménez, S. Esplugas, *Appl. Catal. B: Environ.*, 2004, **47**, 219.
- 22 P. R. Gogate, A. B. Pandit, *Adv. Environ. Res.*, 2004, **8**, 553.
- 23 S. Hemmingsson, B. Holmberg, *Inorg. Chem.*, 1980, **19**, 2242.
- 24 I. Zsigrai, S. Gadžurić, B. Matijević, *Z. Naturforsch.*, 2005, **60a**, 201.

- 25 I. Zsigrai, S. Gadžurić, R. Nikolić, L. Nagy, *Z. Naturforsch.*, 2004, **59a**, 602.
- 26 F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, Vol. 3, John Wiley and Sons, New York, 1988.
- 27 M. Vraneš, S. Gadžurić, I. Zsigrai, *J. Mol. Liq.*, 2007, **135**, 135.
- 28 J. L. Beltran, R. Codony, M. D. Prat, *Anal. Chim. Acta*, 1993, **276**, 441.
- 29 P. Gans, A. Sabatini, A. Vacca, *Talanta*, 1996, **43**, 1739.
- 30 P. Gans, A. Sabatini, A. Vacca, *Ann. Chim.*, 1999, **89**, 45.
- 31 M. Vraneš, S. Gadžurić, I. Zsigrai, *J. Mol. Liq.*, 2009, **145**, 14.
- 32 H. W. Smith, W. J. Stratton, *Inorganic Chem.*, 1977, **16**, 1640.
- 33 C. J. Balhausen, C. K. Jørgensen, *Acta Chim. Scand.*, 1955, **9**, 397.
- 34 D. M. Gruen, *J. Inorg. Nucl. Chem.*, 1957, **4**, 74.
- 35 H. A. Øye, D. M. Gruen, *Inorg. Chem.*, 1965, **4**, 1173.
- 36 C. A. Angell, D. M. Gruen, *J. Inorg. Nucl. Chem.*, 1967, **29**, 2243.
- 37 S. Malato, P. Fernández-Ibáñez, M. I. Maldonado, J. Blanco, W. Gernjak, *Catal. Today*, 2009, **147**, 1.

For *Table of contents* use only

Thermochromism, stability and thermodynamics of cobalt(II) complexes in newly synthesized nitrate based ionic liquid and its photostability

Nemanja Banić, Milan Vraneš, Biljana Abramović, János Csanádi and Slobodan Gadžurić

