



# The solvation and electrochemical behavior of copper acetylacetonate complexes in ionic liquids



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## ABSTRACT

The behavior of copper(II) complexes of pentane-2,4-dione and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, [Cu(acac)<sub>2</sub>] (**1**) and [Cu(HFacac)<sub>2</sub>(H<sub>2</sub>O)] (**2**), in ionic liquids and molecular organic solvents, was studied by spectroscopic and electrochemical techniques.

The electron paramagnetic resonance characterization (EPR) showed well-resolved spectra in most solvents. In general the EPR spectra of [Cu(acac)<sub>2</sub>] show higher *g<sub>z</sub>* values and lower hyperfine coupling constants, *A<sub>z</sub>*, in ionic liquids than in organic solvents, in agreement with longer Cu–O bond lengths and higher electron charge in the copper ion in the ionic liquids, suggesting coordination of the ionic liquid anions. For [Cu(HFacac)<sub>2</sub>(H<sub>2</sub>O)] the opposite was observed suggesting that in ionic liquids there is no coordination of the anions and that the complex is tetrahedrally distorted.

The redox properties of the Cu(II) complexes were investigated by cyclic voltammetry (CV) at a Pt electrode (*d* = 1 mm), in bmimBF<sub>4</sub> and bmimNTf<sub>2</sub> ionic liquids and, for comparative purposes, in neat organic solvents. The neutral copper(II) complexes undergo irreversible reductions to Cu(I) and Cu(0) species in both ILs and common organic solvents (CH<sub>2</sub>Cl<sub>2</sub> or acetonitrile), but, in ILs, they are usually more easier to reduce (less cathodic reduction potential) than in the organic solvents. Moreover, **1** and **2** are easier to reduce in bmimNTf<sub>2</sub> than in bmimBF<sub>4</sub> ionic liquid.

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## 1. Introduction

Room temperature ionic liquids (ILs) are nowadays considered good alternatives to volatile organic solvents since they have appealing properties such as very low vapor pressure, high thermal stability, broad liquid temperature range, and high solvation power for a large range of organic compounds and catalysts, including Lewis acids [1]. The coordinating ability of an ionic liquid is a very important property particularly if a catalyst needs to coordinate a substrate for the catalytic reaction to occur. It has been shown that this depends mainly on the ionic liquid anion [2,3]. Several methods have been applied to evaluate the coordination ability of ionic liquid anions, the simplest one being the measurement of the absorption spectra of solvatochromic dyes. These are compounds that are sensitive to specific and/or non-specific interactions with the solvent. Their electronic absorption spectrum changes with the solvent's polarity and several probes have been used to evaluate interactions with ionic liquids, particularly the following transition metal complexes: [Fe(phen)<sub>2</sub>(CN)<sub>2</sub>]ClO<sub>4</sub> [4],

[Cu(acac)(tmen)][BPh<sub>4</sub>] [2,3], [Ni(acac)(tmen)][BPh<sub>4</sub>] [5] and [Mn(NTf<sub>2</sub>)<sub>2</sub>] [6], where phen = 1,10'-phenanthroline, acac = acetylacetonate, tmen = N,N,N',N'-tetramethylethylenediamine, BPh<sub>4</sub> = tetraperfluoroborate and NTf<sub>2</sub> = bis(trifluoromethylsulfonyl)imide.

The lowest energy *d–d* band of the square planar cation [Cu(acac)(tmen)][BPh<sub>4</sub>] can be correlated with solvent donor numbers.[7] The shift in this band results from the *d*-orbital splitting of copper(II) when the complex becomes five or six coordinated. The results for ionic liquids showed that the spectroscopic shift was entirely independent of the nature of the cation and was only dependent on the anion [3]. The basicity order obtained for the studied IL anions was PF<sub>6</sub><sup>-</sup> < NTf<sub>2</sub><sup>-</sup> < OTf<sup>-</sup>. Our group reported on the structural characterization of vanadyl acetylacetonate in imidazolium room temperature ionic liquids, and showed that [VO(acac)<sub>2</sub>] is solvatochromic in the selected ionic liquids and behaves as in molecular organic solvents, suggesting coordination of the ionic liquid anion in the solvents with higher coordinating ability [8]. The Lewis basicity order obtained for the reported ionic liquid anions was PF<sub>6</sub><sup>-</sup> < NTf<sub>2</sub><sup>-</sup> < OTf<sup>-</sup> ≈ MeCO<sub>2</sub><sup>-</sup> < MeSO<sub>4</sub><sup>-</sup> < BF<sub>4</sub><sup>-</sup> ≈ N(CN)<sub>2</sub><sup>-</sup> < Me<sub>2</sub>PO<sub>4</sub><sup>-</sup>, which is similar to the one obtained by Wasserscheid et al. [2].

Bis(acetylacetonato)copper(II), [Cu(acac)<sub>2</sub>], is a very common and stable transition metal complex. It is quite easy to prepare

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and shows simple magnetic and spectral properties. This paper reports an investigation on the effect of the solvent, in particular ionic liquids, on the visible absorption spectra and on the electron paramagnetic resonance (EPR) parameters of  $[\text{Cu}(\text{acac})_2]$  and  $[\text{Cu}(\text{HFacac})_2(\text{H}_2\text{O})]$  [HFacac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione]. These complexes are soluble in a wide variety of organic solvents, in contrast to the copper halides, and therefore are good probes to evaluate the solvation ability of the ionic liquids. Moreover, its electrochemical behavior in selected ionic liquids is also studied. Neat organic solvents were used for comparison purposes.

The X-ray structure of  $[\text{Cu}(\text{acac})_2]$  [9–11] shows the two acetylacetonate molecules chelated to the copper ion by the four oxygen atoms, which are located on the plane. The symmetry of the molecule is  $D_{2h}$  (sometimes approximated as  $D_{4h}$ ), and all copper-oxygen distances are identical. On the other hand, the crystal structure of anhydrous  $[\text{Cu}(\text{HFacac})_2]$  contains square-planar molecules with close intermolecular Cu–F contacts [12,13].

It is known that the bonding in a complex can be strongly influenced by the nature of the surroundings, namely the solvent. EPR is a helpful spectroscopic tool for the evaluation of the coordination in paramagnetic metal complexes. Copper(II) has an unpaired electron in a  $d^9$  electronic configuration with a nuclear spin of  $3/2$  (for the two stable isotopes  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ ). The spin Hamiltonian parameters –  $g$  value and hyperfine coupling constant,  $A$  – are strongly influenced by the ligand donor atoms. Moreover, coordination of solvent molecules or anions in the apical positions of square planar copper complexes, increases the Cu-donor atom bond length, decreasing the  $A_z$  value and increasing the  $g_z$  value [14].

In this report we present the structural characterization of  $[\text{Cu}(\text{acac})_2]$  and  $[\text{Cu}(\text{HFacac})_2]$  by Vis and EPR spectroscopies, and electrochemistry, in organic solvents and ionic liquids. Well-resolved EPR spectra were obtained in most solvents.

## 2. Results and discussion

### 2.1. Characterization of the ionic liquids

The ionic liquids chosen for this study are constituted by the ions shown in Scheme 1. They are mainly derived from bmim<sup>+</sup> (1-butyl-3-methylimidazolium) with different anions. For the sake of cation comparison bmpyNTf<sub>2</sub> (bmpy<sup>+</sup> = 1-butyl-3-methylpyrrolidinium) was also used. The preparation and spectral data for the ionic liquids have been described elsewhere [8,15]. The procedure used in the preparation and/or purification is able to afford colorless liquids, suitable for spectroscopic studies. The analytic characterization showed the absence of impurities, such as residual chloride, which could change the solvation properties. Before using, these ILs were dried for at least 48 h in vacuum at 50 °C. The water content was measured by Karl Fischer coulometer analysis. For hydrophobic ILs the values did not exceed 400 ppm, but for the most hygroscopic they can reach 3100 ppm, which in terms of water concentration corresponds to 0.18 M.

### 2.2. Characterization of the copper(II) complexes

The copper(II) complexes were prepared according to literature procedures [16] and their characterization (elemental analysis and FTIR) confirmed the formulation. The copper bis-hexafluoroacetylacetonate complex may be obtained as the dark blue–violet anhydrous, the blue–green  $[\text{Cu}(\text{HFacac})_2(\text{H}_2\text{O})]$  or the yellow–green  $[\text{Cu}(\text{HFacac})_2(\text{H}_2\text{O})_2]$  complex [13,17]. The assignment of the number of water molecules for the prepared complex is not straightforward: the color (yellow–green) suggests the presence of two water molecules, however the carbon content (24.3%) fits

the  $[\text{Cu}(\text{HFacac})_2(\text{H}_2\text{O})]$  formulation (theoretical value 24.3%), which was the one used throughout the work.

The electronic absorption spectra of the complexes were measured in organic solvents and the obtained spectra are included in Supporting Information (SI). Being a  $d^9$  metal ion, copper is subject to Jahn-Teller distortion. In square planar or octahedral complexes the unpaired electron occupies the  $d_{x^2-y^2}$  orbital, which has its lobes pointing directly to the equatorial ligands, along the  $x$  and  $y$  axes of the molecule. The absorption spectra of the compounds shows 2 or 3 bands in the Vis region (in some cases they are overlapped) which can be attributed to the promotion of the electrons in the lower energy orbitals to the hole in  $d_{x^2-y^2}$  orbital of the copper(II) ion. We tried to correlate the low energy absorption maximum with the Kamlet-Taft [18–21] (KT) solvent parameters. Although in most cases the fitting parameters were not satisfactory, there were clear correlations with  $\beta$ , the hydrogen bond basicity, for  $[\text{Cu}(\text{HFacac})_2]$ , which is known for becoming 5 or 6-coordinated in donating solvents:

$$\lambda_{\text{max}} = 680 \pm 5 + 36 \pm 9 \times \beta \quad (r^2 = 0.70)$$

In ionic liquids no clear correlation with the KT solvent parameters was observed. This suggests that either the solvation process depends on several parameters (and as the number of solvents used was limited, it was not possible to obtain any correlation with more than one parameter) or that the presence of different amounts of residual water in the ionic liquids affects its solvation properties, and therefore the KT parameters, which has been shown by other authors [22–24]. Fig. 1 shows the absorption spectra obtained for complex  $[\text{Cu}(\text{HFacac})_2(\text{H}_2\text{O})]$  in selected ionic liquids.  $[\text{Cu}(\text{acac})_2]$  is only soluble in the ILs containing the anions with the higher coordinating power, e.g.  $\text{N}(\text{CN})_2^-$  [8]. The fluorinated complex is sparingly soluble in a wide range of ILs. Therefore, the most solvatochromic complex in the selected ILs is  $[\text{Cu}(\text{HFacac})_2(\text{H}_2\text{O})]$ , for which a variation of ca. 190 nm in the position of the absorption maximum for the lower energy band was observed. Table 1 presents the data, which is included in graphical form in the supporting information.

### 2.3. EPR in organic solvents

The EPR spectra of  $[\text{Cu}(\text{acac})_2]$  (1) in organic solvents were measured both at room temperature and 77 K, while those of  $[\text{Cu}(\text{HFacac})_2(\text{H}_2\text{O})]$  (2) were measured only at 77 K. All spectra were simulated using a program developed by Rockenbauer and Korecz [25]. The EPR spectra measured at room temperature for  $[\text{Cu}(\text{acac})_2]$  (see SI) present the expected four-line pattern and the line widths change with the nuclear quantum number ( $m_I$ ), with the high field line being narrower and more intense than the lower field lines. In some solvents the isotropic spectra from the monomer is superimposed on an isotropic singlet ( $\Delta M_s = \pm 1$ ) from copper clusters (e.g. in DMSO). The inclusion of this “background” signal in the simulation improved the quality of the fit. Table 2 presents the spin Hamiltonian parameters obtained. The values are in good agreement with data from the literature [26] and it was possible to correlate the spin Hamiltonian isotropic parameters ( $g_{\text{iso}}$  and  $A_{\text{iso}}$ ) with the solvent basicity ( $\beta$ ) (see SI):

$$g_{\text{iso}} = 2.1206 \pm 0.005 + 0.030 \pm 0.008 \times \beta \quad (r^2 = 0.757)$$

$$A_{\text{iso}} = 79 \pm 5 - 25 \pm 9 \times \beta \quad (r^2 = 0.651)$$

In general, the higher the solvent basicity, the longer the Cu–O bonds and therefore the higher the electron density in the copper ion, which leads to an increase in the  $g$ -value and a decrease in the hyperfine coupling constant,  $A$ , as expected [14].

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