Inorganica Chimica Acta 409 (2014) 465–471

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

The solvation and redox behavior of mixed ligand copper(II) complexes of acetylacetonate and aromatic diimines in ionic liquids

Patrique Nunes [a], Nóra V. Nagy [b], Elisabete C.B.A. Alegria [a,c], Armando J.L. Pombeiro [a], Isabel Correia [a,*]

[a] Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisbon, Portugal
[b] Institute of Molecular Pharmacology, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Pusztaszeri út 59-67, H-1025 Budapest, Hungary
[c] Área Departamental de Engenharia Química, ISEL, R. Conselheiro Emídio Navarro, 1950-062 Lisbon, Portugal

ARTICLE INFO

Article history:
Received 12 August 2013
Received in revised form 20 September 2013
Accepted 23 September 2013
Available online 5 October 2013

Keywords:
Cationic copper complexes
Ionic liquids
EPR
Cyclic voltammetry

ABSTRACT

The behavior of two cationic copper complexes of acetylacetonate and 2,2′-bipyridine or 1,10-phenanthroline, [Cu(acac)(bipy)]Cl (**1**) and [Cu(acac)(phen)]Cl (**2**), in organic solvents and ionic liquids, was studied by spectroscopic and electrochemical techniques. Both complexes showed solvatochromism in ionic liquids although no correlation with solvent parameters could be obtained. By EPR spectroscopy rhombic spectra with well-resolved superhyperfine structure were obtained in most ionic liquids. The spin Hamiltonian parameters suggest a square pyramidal geometry with coordination of the ionic liquid anion. The redox properties of the complexes were investigated by cyclic voltammetry at a Pt electrode (d = 1 mm) in $bmimBF_4$ and $bmimNTf_2$ ionic liquids. Both complexes **1** and **2** are electrochemically reduced in these ionic media at more negative potentials than when using organic solvents. This is in agreement with the EPR characterization, which shows lower A_z and higher g_z values for the complexes dissolved in ionic liquids, than in organic solvents, due to higher electron density at the copper center. The anion basicity order obtained by EPR is NTf_2^-, $N(CN)_2^-$, $MeSO_4^-$ and $Me_2PO_4^-$, which agrees with previous determinations.
© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Room temperature ionic liquids (ILs) are considered alternative substitutes to volatile organic solvents due to having attractive properties, such as very low vapor pressure, high thermal stability, broad liquid range, and high solvation power, as observed for a broad range of organic compounds and catalysts, which include Lewis acids [1]. In catalysis, the coordination ability of the ionic liquid is essential since in many catalytic reactions the transition metal complex needs to coordinate the substrate for the reaction to occur. It has been shown that this mainly relates to the ionic liquid anion [2,3]. Many techniques have been used to study the coordination ability of the ionic liquid anion, the simplest one being the measurement of the absorption spectra of solvatochromic dyes. Particularly, the following transition metal complexes have been used as solvatochromic probes: $[Fe(phen)_2(CN)_2]ClO_4$ [4], [Cu(acac)(tmen)][BPh_4] [2,3], [Ni(acac)(tmen)][BPh_4] [5] and $[Mn(NTf_2)_2]$ [6], where phen = 1,10-phenanthroline, acac = acetylacetone, tmen = N,N,N′,N′-tetramethylethylenediamine, BPh_4 = tetraphenylborate and NTf_2 = bis(trifluoromethylsulfonyl)imide [7].

For [Cu(acac)(tmen)][BPh_4] electronic absorption bands in the visible range can be correlated with solvent donor numbers [8]. A shift in the lowest energy band observed in the Visible range is a result of the d-orbital splitting of copper(II) when this ion becomes penta- or hexa-coordinated. In ionic liquids the shift was independent of the nature of the cation and was only dependent on the IL anion [3]. A basicity order was obtained for the IL anions studied: $PF_6^- < NTf_2^- < OTf^-$.

Our group reported on the structural characterization of $[VO(acac)_2]$ in imidazolium ionic liquids, and showed that the vanadium complex is solvatochromic in the selected ionic liquids and behaves as in organic solvents, indicating coordination of the anion in the solvents with higher coordinating ability [9]. The order of Lewis basicity obtained in this study was $PF_6^- < NTf_2^- < OTf^- \approx MeCO_2^- < MeSO_4^- < BF_4 \approx N(CN)_2^- < Me_2PO_4^-$ that is similar to the one obtained by Wasserscheid et al. [2].

In this paper we take our studies further and investigate the effect of the solvent on the spectral properties and EPR parameters of mixed cationic complexes containing acetylacetonate and aromatic diimines. These type of complexes, generally known as CASIOPEINAS®, have been widely studied due to their potentially useful pharmacological properties, such as cytotoxic and antineoplastic [10,11]. However, their characterization in solution is still underdeveloped. Moreover, ionic liquids are being considered as alternative pharmaceutic solvents for poorly water-soluble model drugs [12] and also as Active Pharmaceutical Ingredients [12,13]. Therefore, the structural characterization of the selected copper complexes in ionic liquids is an important issue.

* Corresponding author. Tel.: +351 218419264; fax: +351 21846445.
E-mail address: icorreia@ist.utl.pt (I. Correia).

0020-1693/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ica.2013.09.040

Several X-ray structures have been published for cationic mixed ligand copper(II) complexes of the type [Cu(acac)(NN)]X, in which NN is 1,10-phenanthroline (phen) or 2,2′-bipyridine (or a derivative) and X is an anion [14–19]. The X-ray structures of two complexes containing acac and phen (or 2,9-dimethyl-1,10-phenanthroline) and NO_3^- as counterion, show that in both complexes the copper atom has an approximate square pyramidal coordination geometry [16]. Another phen complex, in which the counterion is ClO_4^-, shows the same geometry, also with the anion occupying the axial position [17]. A structure containing water in the axial position and NO_3^- as counterion was found for $[Cu(acac)(bipy)(H_2O)]NO_3$, while for the analogous 1,10-phenanthroline complex the Br^- occupied the axial position, instead of the water molecule [18]. Complexes containing the bulky BPh_4^- show coordination of solvent molecules in the apical position [19].

It is well known that the chemical bonding in a compound is influenced by the solvent. Electron paramagnetic resonance (EPR) is a valuable spectroscopic tool for the determination of the coordination environment in paramagnetic metal complexes. Copper(II), having one unpaired electron in a d^9 electronic configuration and a nuclear spin of 3/2 (for both ^{63}Cu and ^{65}Cu, the most abundant isotopes) is a suitable metal ion to be studied by this technique. Also, the copper(II) unpaired electron occupies an orbital which points directly to the equatorial ligands, therefore, often interaction of the electron with the nuclear spin of donor atoms such as ^{14}N is observed, providing a way to determine the ligand environment around the Cu(II) metal center in solution.

In this report we characterize [Cu(acac)(bipy)]Cl and [Cu(acac)(phen)]Cl [bipy = 2,2′-bipyridine and phen = 1,10-phenanthroline] structurally by optical absorption and EPR spectroscopies, and cyclic voltammetry in molecular organic solvents and ionic liquids.

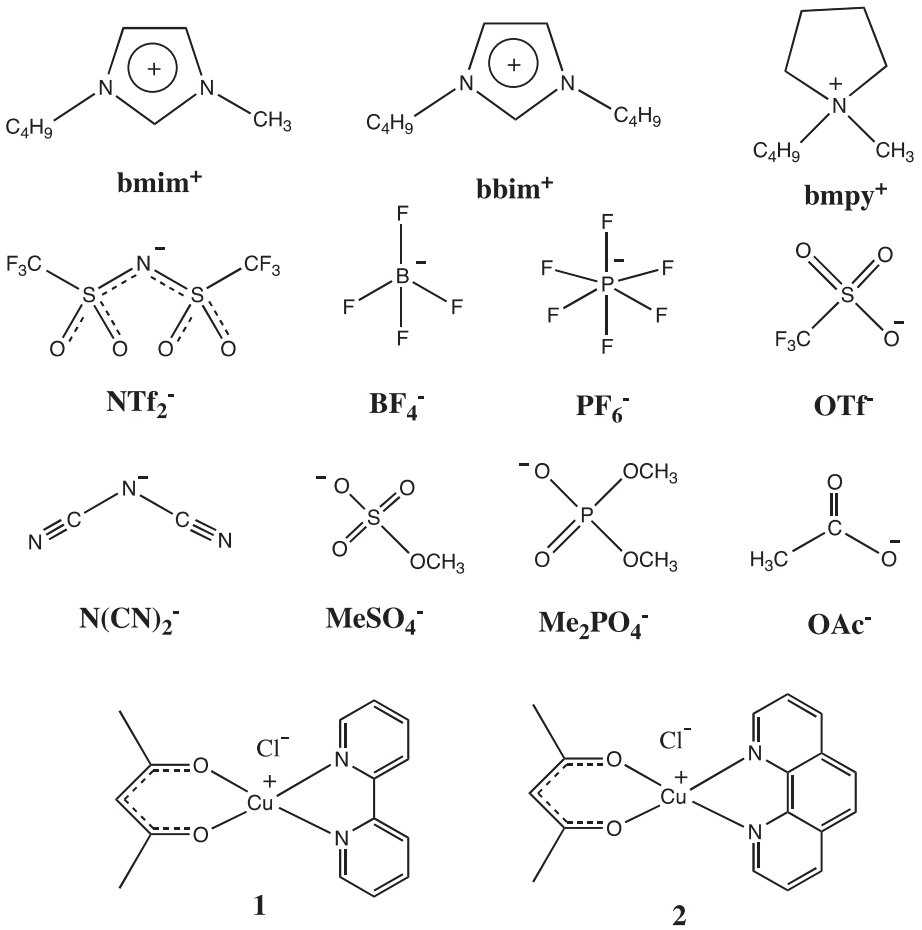
2. Results and discussion

2.1. Characterization of the ionic liquids

The component ions of ionic liquids chosen for this study are shown in Scheme 1. The cations include: $bmim^+$ (1-butyl-3-methylimidazolium), $bbim^+$ (1-butyl-3-butylimidazolium) and $bmpy^+$ (1-butyl-1-methylpyrrolidinium); and the anions include: NTf_2^- [bis(trifluoromethylsulfonyl)imide], OTf^- (trifluoromethanesulfonate), BF_4^- (tetrafluoroborate), PF_6^- (hexafluorophosphate), $N(CN)_2^-$ (dicyanamide), $Me_2PO_4^-$ (dimethylphosphate), $MeSO_4^-$ (methylsulphate) and OAc^- (acetate). The preparation and spectral data for these ionic liquids have been described elsewhere [20]. The procedure used in the preparation and purification yielded colorless liquids and the chemical analysis indicates the absence of impurities, such as residual chloride, which can change solvation properties. Before using 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 (*e.g.*, $bmimBF_4$) the values did not exceed 350 ppm, but for the most hygroscopic they are *ca.* 1500 ppm, which in terms of water concentration corresponds to 0.08 M.

2.2. Characterization of the copper(II) complexes

The copper(II) complexes (see Scheme 1) were prepared by mixing the ligands and $CuCl_2$ in alcohol. The structural characterization



Scheme 1. Ionic liquid's cations and anions and formula of the complexes.

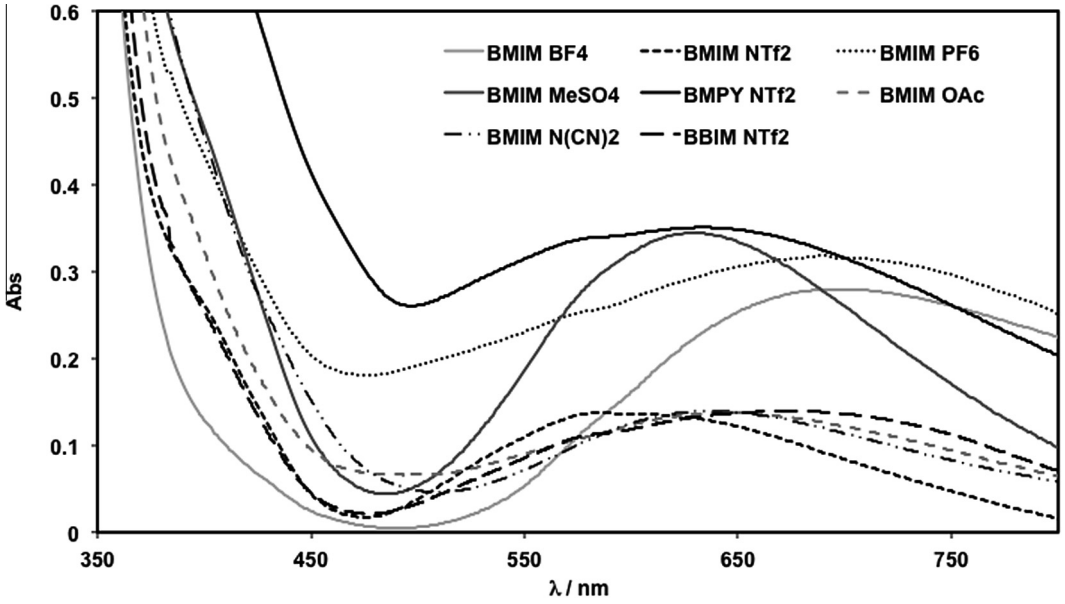


Fig. 1. Absorption spectra for [Cu(acac)(bipy)]Cl in selected ionic liquids. Complex concentration is *ca.* 3 mM and path length is 1 cm. The spectrum in bmimMeSO$_4$ was obtained at 50 °C due to the higher melting point of this IL.

by elemental analysis and FTIR (data included in the Section 4) confirmed their formulation.

These complexes were also characterized using electronic absorption spectroscopy, with their spectra measured in several organic solvents, which are included in the Supporting Information (SI). Overall, the complexes show two or three bands in the visible and, in some cases, they overlap. Being a $3d^9$ metal center, copper(II) is subject to Jan-Teller distortion. In square planar or octahedral complexes the unpaired electron occupies the d_{x2-y2} orbital, which has its lobes pointing directly to the equatorial ligands, along *x* and *y* axes of the molecule. The correlation of the low energy absorption maximum with the Kamlet Taft (KT) solvent parameters in organic solvents, showed that although in most cases the fitting parameters were not satisfactory, there were clear correlations with α, the hydrogen bond acidity (see SI1).

In ionic liquids no clear correlation with the KT solvent parameters was observed. Fig. 1 shows absorption spectra obtained for [Cu(acac)(bipy)]Cl (**1**) in selected ionic liquids. Both complexes are soluble in most ILs, and the most solvatochromic complex is complex **1**, for which a variation of *ca.* 170 nm in the position of the absorption maximum for the lower energy band is observed. Table 1 summarizes the collected data, which are also included in graphical form in the Supporting Information.

2.3. EPR characterization

The EPR spectra of [Cu(acac)(bipy)]Cl (**1**) in organic solvents were measured both at room temperature and 77 K. The EPR spectra of [Cu(acac)(phen)]Cl (**2**) were measured only at 77 K. All spectra were simulated using a program developed by Rockenbauer and Korecz [21], and figures with the experimental and simulated EPR spectra are included in the SI section. At room temperature, the spectra for complex **1** present the expected four-line pattern and the line widths change with m_I, with the high field line being narrower and more intense than the lower field lines. Table 2 presents optimized sets of spin Hamiltonian parameters obtained by simulation.

The anisotropic EPR spectra obtained at 77 K are better resolved and more informative. The unpaired electron of the copper ion occupies a d-orbital that points directly towards equatorial ligands and consequently can couple magnetically with the nuclear spin of ^{14}N donor atoms. This is known as superhyperfine (shf) coupling interaction. So, when a nitrogen atom is coordinated to Cu(II) an additional splitting of hyperfine lines may be observed. Each hyperfine signal is split into $2n + I$ signals, where I is the nuclear magnetic moment and n is the number of the corresponding nuclei. Thus, a ^{14}N donor gives rise to an 1:1:1 triplet, while two ^{14}N donors yield a 1:2:3:2:1 quintet. When present, this shf structure is visible in the *xy* component, as the *z* component is usually undetected due to strong line broadening. However, for the studied complexes, in some cases the shf coupling was observed in both components: *e.g.*, for [Cu(acac)(bipy)]Cl in ethanol (see SI, Fig. SI5) and in bbimNTf$_2$.

Most of the EPR spectra were simulated considering rhombic symmetry for *g* and *A* tensors; and when shf structure was present, rhombic shf tensors were used for the coupled nitrogen atoms. The EPR spectra observed in CH_3CN, H_2O and DMSO were not resolved, and only a singlet was observed, due to strong magnetic interactions between the copper centers. In EtOH the spectrum is well resolved and shf coupling is observed also in the parallel region. The simulation of these EPR spectra yielded the

Table 1
Wavelength (nm) of the lowest energy absorption band of the complexes in organic solvents and ionic liquids.

Solvent/Complex	[Cu(acac)(bipy)]Cl	[Cu(acac)(phen)]Cl
DMSO	635	700
DMF	696	725
Pyridine	741	–
$CHCl_3$	696	710
Acetone	–	640
1-BuOH	–	645
CH_3CN	–	712
EtOH	725	640
H_2O	611	617
bmimN(CN)$_2$	639	–
bmimOAc	643	662
bmimBF$_4$	700	720
bmimMeSO$_4$	632	648
bmimPF$_6$	706	699
bmimNTf$_2$	804	678
bmpyNTf$_2$	638	–

Table 2
Spin Hamiltonian parameters of the EPR spectra obtained by simulation for complexes [Cu(acac)(bipy)]Cl **1** and [Cu(acac)(phen)]Cl **2**. Hyperfine coupling constants, A, in $\times 10^4$ cm^{-1}.

Solvent	g_x (or $g_\perp$)	g_y	g_z (or $g_\parallel$)	A_x (or $A_\perp$)	A_y	A_z ($A_\parallel$)	g_0	A_0
[Cu(acac)(bipy)]Cl								
$CHCl_3$	2.0755	2.0495	2.2518	35.2	29.1	178.5	2.1381	55.8
DMF	2.0580	2.0370	2.2680	14.4	16.2	171.5	2.1233	72.5
	2.0585	2.0300	2.2467	15.2	23.7	183.6		
EtOH	2.0609	2.0445	2.2536	10.7	21.2	184.2	2.1354	67.9
Pyridine	2.0546		2.5538	11.3		203.1	2.1458	53.9
CH_3CN	2.0386		2.2100				2.1183	79.4
H_2O	2.0639		2.1890				2.1243	73.7
DMSO	2.1217		2.2996				2.1370	82.4
bmimOAc	2.0582	2.0429	2.3118	21.1	14.9	170.1		
$bmimMeSO_4$	2.0642	2.0461	2.2560	22.0	18.1	170.3		
$bmimMe_2PO_4$	2.0607		2.2594	18.5		172.6		
$bmimBF_4$	2.0559		2.2562	21.7		172.8		
$bmimN(CN)_2$	2.0609	2.0433	2.2517	21.3	19.5	177.4		
$bmimPF_6$	2.0523	2.0407	2.2450	28.9	27.9	178.3		
$bbimNTf_2$	2.0566	2.0423	2.2458	21.9	28.5	180.0		
$bmpyNTf_2$	2.0576	2.0422	2.2469	19.2	33.2	180.5		
$bmimNTf_2$	2.0573	2.0423	2.2403	19.4	26.8	188.4		
[Cu(acac)(phen)]Cl								
1-BuOH	2.0593	2.0538	2.2574	33.4	0.1	179.1		
Acetone	2.0563	2.0485	2.2563	32.8	3.4	179.6		
Pyridine	2.0580		2.2586	17.0		176.8		
EtOH	2.0571	2.0494	2.2592	28.0	3.5	181.6		
H_2O	2.0833		2.1234					
DMSO	2.0774		2.1421					
$bmimBF_4$	2.0674	2.0581	2.2487	0	47.2	156.7		
bmimOAc	2.0587	2.0433	2.3086	20.9	14.4	163.7		
$bmimMeSO_4$	2.0672	2.0435	2.2605	0.8	20.7	167.2		
$bmpyNTf_2$	2.0633	2.0558	2.2595	0	31.3	169.3		
$bmimNTf_2$	2.0447	2.0289	2.2249	0	43.0	175.8		

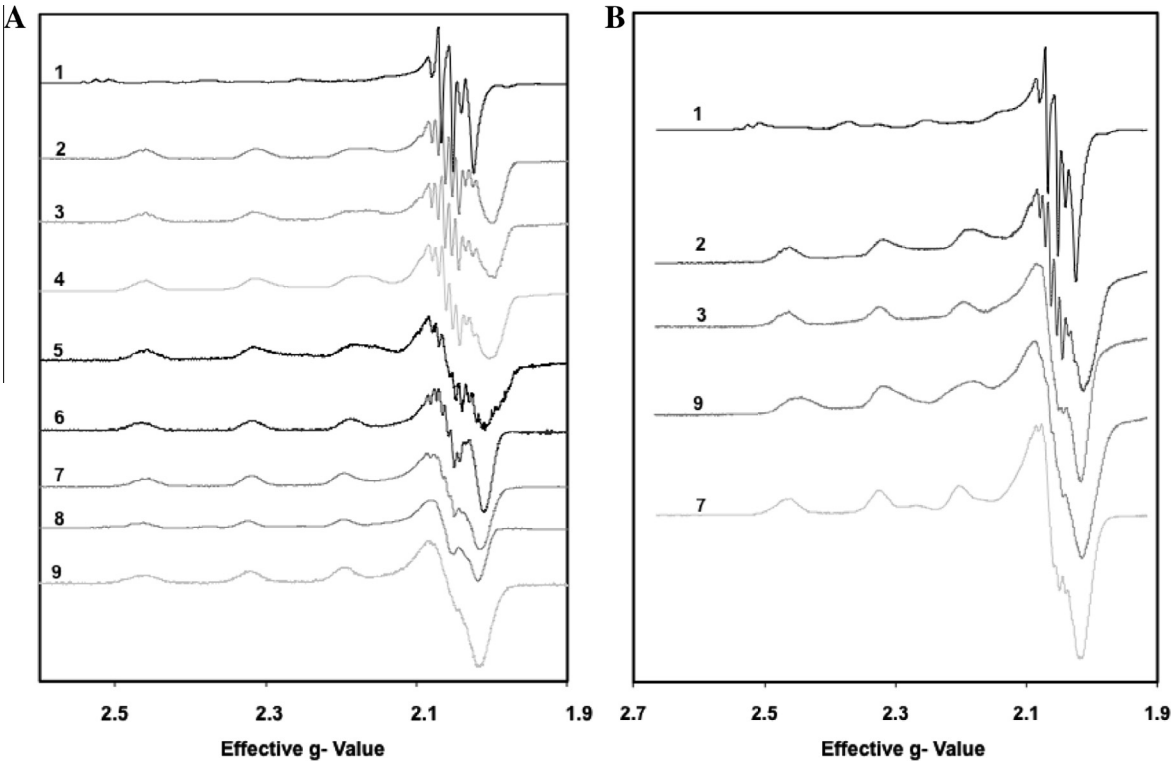


Fig. 2. X-band EPR spectra obtained at 77 K for (A) complex **1**, [Cu(acac)(bipy)]Cl and (B) complex **2**, [Cu(acac)(phen)]Cl, in selected ionic liquids. 1 – bmimOAc, 2 – $bmimNTf_2$, 3 – $bmpyNTf_2$, 4 – $bbimNTf_2$, 5 – $bmimPF_6$, 6 – $bmimN(CN)_2$, 7 – $bmimMeSO_4$, 8 – $bmimMe_2PO_4$ and 9 – $bmimBF_4$.

spin-Hamiltonian parameters given in Table 2. These are in agreement with published values for similar complexes [14,17]. In DMF complex **1** exhibits two species. We were able to simulate both of them, however the assignments are not straightforward. The species with the higher A_z is attributed to the product of complex solvolysis.

EPR spectra of the same two copper complexes in ionic liquids were observed at 77 K. Fig. 2 presents the spectra and the spin-Hamiltonian parameters are given in Table 2. At first glance the EPR spectra correspond to axial g and A tensors, but the symmetry of the complexes is in fact lower and simulation with rhombic parameters yielded better agreement in most cases. These EPR spectra exhibit well-resolved hyperfine and superhyperfine structure in the parallel ($B_{//}2$) (in some ILs) and perpendicular ($B\perp2$) components (where B is the magnetic field): in the parallel region three of four hyperfine bands are well resolved, while the fourth band overlaps g_z features. Other EPR spectra exhibit similar features (except in bmimOAc) and in particular the EPR spectra obtained in ILs containing the NTf_2^- anion exhibit high-resolution superhyperfine structure in the $B\perp2$ resonances. However, in these ILs (and **1** in $bmimPF_6$ and **2** in $bmimBF_4$) an extra resonance line appears at $g\approx1.8$ possibly from dimer species. However, at $g\approx4$ no forbidden spin transitions ($\Delta M_S = \pm 2$, magnetic dipolar coupling between copper centers) were observed.

Fig. 3 presents the experimental and simulated spectra of complex **1** in $bmimN(CN)_2$. The shf structure was simulated assuming spin coupling with two equatorial ^{14}N neighbors. The bigger N coupling corresponds to a nitrogen's hf tensor's principal axis pointing towards the copper ion. Since one of them has a large coupling (a_x) in the *x*-axis and the other one has it (a_y) in the *y*-axis, for example, complex **1** in $bmpyNTf_2$ exhibits shf coupling constants $a_x = 5.64$ G, $a_y = 15.19$ G and $a_z = 5.57$ G for N_1, and $a_x = 15.19$ G, $a_y = 6.71$ G and $a_z \sim 0$ G for N_2.

Overall, A_z coupling constant was systematically lower in ionic liquids than in organic solvents, whereas the opposite was observed for g_z value. Upon solvent coordination, the copper-donor atom bond elongates, lowering the delocalization of the electron density, and increasing density at the copper atom. This is reflected in the spin Hamiltonian parameters, particularly in a decrease in A_z and an increase in g_z. Thus, our ionic liquids show higher coordinating power than organic solvents.

Fig. 4 shows the correlation between g_z and A_z for both complexes. Except for complex **1** in bmimOAc and complex **2** in $bmimBF_4$ good correlations were obtained. Solvents in the low right end of the graph show higher basicity, and solvents in the high left end show lower basicity. Regardless of the cation (bbim, bmim or bmpy), the NTf_2^- anion shows lower basicity, followed by $N(CN)_2^-$, $MeSO_4^-$ and $Me_2PO_4^-$. For $bmimBF_4$ no straightforward conclusion can be drawn since BF_4^- is an anion that while having a considerable coordination power yet, on account of its water affinity, falls out of the correlations. The problem with bmimOAc is that more than one species is observed in the EPR spectra, since acetate can yield polymeric complexes of copper ions.

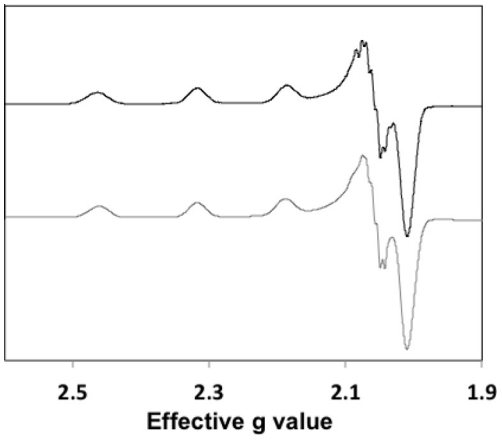


Fig. 3. Experimental and simulated EPR spectra of complex **1**, [Cu(acac)(bipy)]Cl, in $bmimN(CN)_2$. Gray line: experimental spectrum, black line: simulated spectrum.

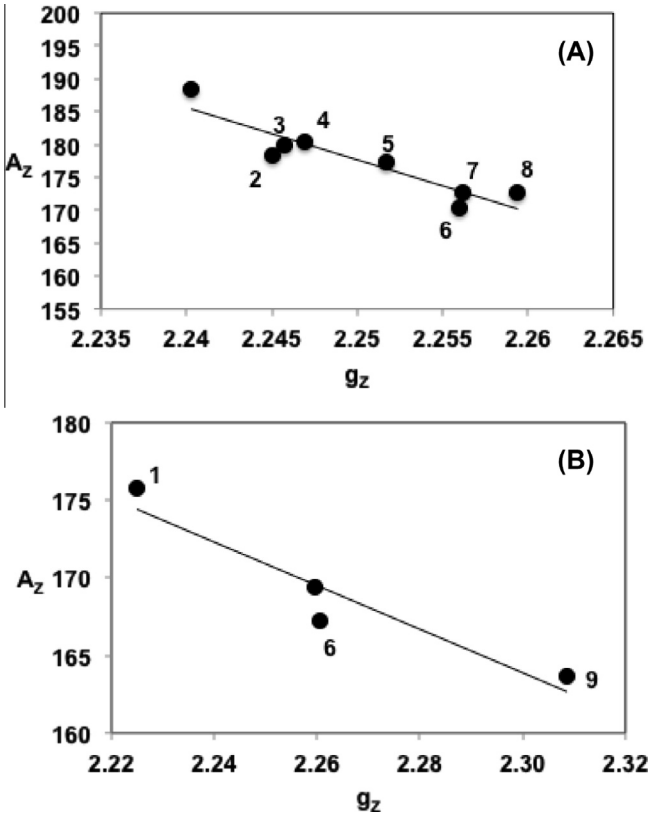


Fig. 4. A_z and g_z correlation between the spin Hamiltonian parameters for copper complexes. (A) [Cu(acac)(bipy)]Cl (**1**) $r^2 = 0.850$ and (B) [Cu(acac)(phen)]Cl (**2**) $r^2 = 0.898$. (1) $bmimNTf_2$, (2) $bmimPF_6$, (3) $bbimNTf_2$, (4) $bmpyNTf_2$, (5) $bmimN(CN)_2$, (6) $bmimMeSO_4$, (7) $bmimBF_4$, (8) $bmimMe_2PO_4$ and (9) bmimOAc.

In complex **2** the hyperfine coupling constant A_z is considerably lower than in complex **1** (see Table 2). Phenanthroline and bipyridine have similar electron-donor properties but phenanthroline is a more rigid ligand. Therefore, the coordination to Cu might be less efficient in phen, due to steric constraints, elongating the Cu-donor atom bonds and decreasing the coupling constant A_z.

2.4. Redox behavior of the complexes

We first studied the cyclic voltammetry of neat $bmimBF_4$ and $bmimNTf_2$, using a platinum disk working electrode ($d = 1$ mm), at room temperature. A broad reduction wave was observed at *ca.* −1.9 V *vs.* FcH/FcH^+, probably due to the reduction of species produced in the cathodic limit, usually determined by the organic cation ($bmim^+$) [22,23]. Upon scan reversal, following the cathodic process, a new oxidation wave is observed at $E_p = 0.5$ V *vs.* FcH/FcH^+, corresponding to the oxidation of a species formed at the cathodic process. The study shows that $bmimBF_4$ and $bmimNTf_2$ are electrochemically stable in a wide potential range, suitable for the investigation of our complexes **1** and **2**, in accordance with previous observations [23–25].

The Cu(II) complexes exhibit one first irreversible reduction process (wave $\mathbf{I^{red}}$) at $^{I}E_p^{red} = -0.86$ or −0.87 V *vs.* FcH/FcH^+ for **1** or **2**, respectively, in $bmimNTf_2$ (Fig. 5), or, at the potential of $^{I}E_p^{red} = -0.85$ or −0.82 V *vs.* FcH/FcH^+ for **1** or **2** in $bmimBF_4$, respectively (Fig. 6). This first cathodic wave is followed, at a lower potential, by a second irreversible one (wave $\mathbf{II^{red}}$) at $^{II}E_p^{red} = -1.20$ or −1.18 V *vs.* FcH/FcH^+ for **1** or **2**, respectively, in $bmimNTf_2$, or at $^{II}E_p^{red} = -1.23$ and −1.21 V *vs.* FcH/FcH^+ for **1** or **2**, respectively, in $bmimBF_4$ (Figs. 5 and 6). Moreover, a third irreversible reduction process is observed at *ca.* −1.6 V *vs.* FcH/FcH^+. These cathodic

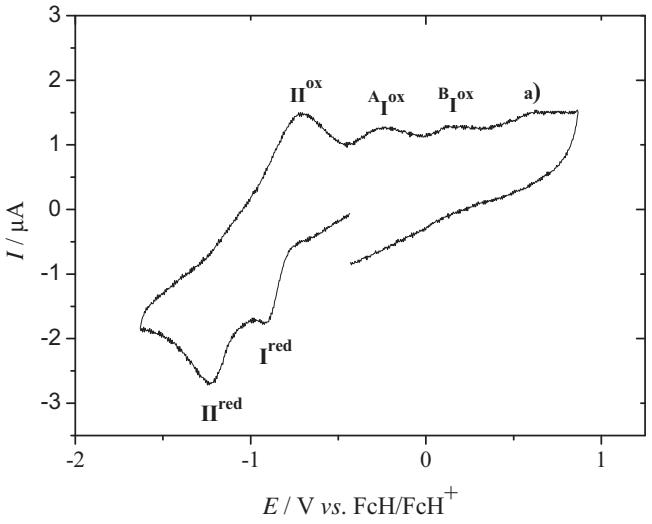


Fig. 5. Cyclic voltammogram of complex **1**, at a Pt electrode, initiated by the cathodic sweep, in $bmimNTf_2$ ($v = 200$ mVs^{-1}). [Complex **1**] = 5.1 mM. *I*: current function and *E*: applied potential. [a]This wave corresponds to oxidation of Cl^- counter-ion.

processes ($\mathbf{I}^{red}$ and $\mathbf{II}^{red}$) are believed to correspond to the $Cu^{II} \rightarrow Cu^{I}$ and $Cu^{I} \rightarrow Cu^{0}$ reductions [7,26–30].

The solutions of complexes **1** and **2** also exhibit one irreversible oxidation wave which is attributed to the oxidation of the chloride counter-ion, its potential value (*ca.* 0.6–0.8 V *vs.* FcH/FcH^+) being consistent with those observed for the oxidation of the same counter-ion in other ILs [31]. This is also supported by the independently determined value, in our study, of the irreversible oxidation wave of benzyltriethylammonium chloride under the same experimental conditions, in $bmimBF_4$ ($E_p^{ox} = 0.78$ V *vs.* FcH/FcH^+) and $bmimNTf_2$ ($E_p^{ox} = 0.81$ V *vs.* FcH/FcH^+).

Upon scan reversal, following the cathodic waves of complexes **1** and **2**, new waves appear (Figs. 5 and 6) due to the oxidation of species formed in the cathodic processes.

The similarity of the first reduction potentials observed for **1** and **2** is consistent with the identical electron-donor character of the 2,2′-bipyridine (bipy) and 1,10-phenantroline (phen) ligands. In fact, these two ligands exhibit the same value (0.26 V *vs.* NHE) [32–34] of the electrochemical Lever E_L parameter, which is a measure of the electron-donor ability of a ligand [32–34] (the stronger

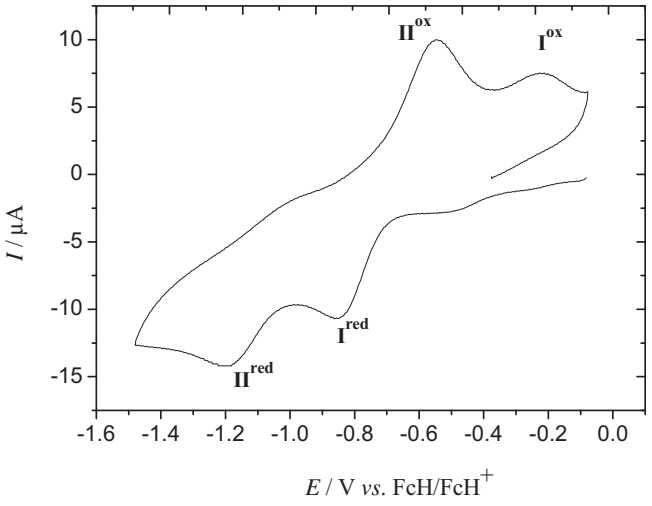


Fig. 6. Cyclic voltammogram of complex **1**, at a Pt electrode, initiated by the cathodic sweep, in $bmimBF_4$ ($v = 200$ mVs^{-1}). [Complex **1**] = 50 mM. *I*: current function and *E*: applied potential.

Table 3
Cyclic voltammetric data[a] for the complexes [Cu(acac)(bipy)]Cl **1** and [Cu(acac)(phen)]Cl **2**.

Solvent	$^{I}E_p^{red}$ ($\mathbf{I}^{red}$)	$^{II}E_p^{red}$ ($\mathbf{II}^{red}$)
[Cu(acac)(bipy)]Cl **1**		
$bmimNTf_2$	−0.86	−1.20
$bmimBF_4$	−0.85	−1.23
CH_2Cl_2	−0.60	−1.02
acetonitrile	−0.78	−1.54
[Cu(acac)(phen)]Cl **2**		
$bmimNTf_2$	−0.87	−1.18
$bmimBF_4$	−0.82	−1.21
CH_2Cl_2	−0.57	−0.93
acetonitrile[b]	−0.55	−0.86

[a] Values in $V \pm 0.02$ relative to FcH/FcH^+ (see Section 4) concerning the cathodic waves $\mathbf{I}^{red}$ and $\mathbf{II}^{red}$; scan rate of 200 mVs^{-1}.
[b] A third cathodic process is observed at $^{III}E_p = -1.26$ V *vs.* FcH/FcH^+.

that character, the lower E_L). Moreover, the considerable lower E_L value of $acac^-$ ($E_L = -0.08$ V) [32–34] is indicative of a stronger electron-donor ability of this anionic ligand in comparison with bipy and phen.

In the 20–1000 mVs^{-1} range (Figs. SI11–SI13) the current intensity (i_p) of the first reduction wave of complexes **1** and **2** is proportional to their concentration, and to the square root of the scan rate ($v^{1/2}$), the constancy of the current-function $i_p v^{-1/2}$ being consistent with the occurrence of a single-electron reduction within this range of scan rates.

For comparative purposes, the redox properties of these two Cu(II) complexes were also investigated by cyclic voltammetry in an organic solvent, *i.e.* in 0.2 M $[^nBu_4N][BF_4]/(CH_2Cl_2)$ solutions, at room temperature, and the measured redox potentials are given in Table 3.

The complexes in these solvents show general electrochemical behaviors that are similar to those observed in the ILs, *i.e.*, two irreversible reduction waves ($\mathbf{I}^{red}$ and $\mathbf{II}^{red}$) which, upon scan reversal, lead to the observation of oxidation waves due to species formed in the cathodic processes (Fig. SI14). The irreversible oxidation wave ($\mathbf{II}^{ox}$) formed upon the second reduction wave ($\mathbf{II}^{red}$) involves the anodic dissolution of the copper deposited during this reduction [26]. This is consistent with electrode passivation upon cathodic controlled potential electrolysis. An irreversible oxidation wave of the chloride counter-ion is observed at E_p^{ox} *ca.* 0.6 V *vs.* FcH/FcH^+, that is consistent with oxidation of benzyltriethylammonium chloride, under the same experimental conditions.

However, the reduction processes for complexes **1** and **2** in the organic solvent occur at reduction potentials that, in almost all cases, are less cathodic (by *ca.* 0.1–0.3 V) than those in the ILs (Table 3), *i.e.*, the copper complexes are more difficult to reduce in the ionic solvents. This is related to slower reduction kinetics [26] in the ILs in comparison with the organic solvents, due to lower diffusion coefficients of the electroactive species in ILs, that are accounted for by the higher viscosity and large size of constituent ions in this ionic medium.

3. Conclusions

Our studies indicate that cationic copper complexes behave similarly in ionic liquids and in molecular organic solvents. In both types of solvents these complexes undergo irreversible reduction to Cu(I) and Cu(0) species, but, in ILs, they reduce at more cathodic potentials than in the organic solvents.

The structural characterization carried out using spectroscopic and electrochemical techniques suggests the involvement of the ionic liquid anion in the solvation of the complexes. The magnetic parameters obtained in ionic liquids are similar to those obtained in alcohols. Overall, our EPR experiments suggest that ionic liquids

have higher coordinating ability than organic solvents, which also accounts for a greater difficulty of electrochemical reduction in ionic liquids. The following anionic basicity order was obtained: $NTf_2^- > N(CN)_2^- > MeSO_4^- > Me_2PO_4^-$.

4. Experimental

4.1. Materials and reagents

All chemicals used were of analytical reagent grade. 1-Methylimidazole was purchased from Acros Organics and distilled over potassium hydroxide; 1-chlorobutane was purchased from Acros Organics and distilled over phosphorus pentoxide. Lithium bis(trifluoromethylsulfonyl)imide [Li(NTf_2)] and lithium trifluoromethanesulfonate [Li(OTf)] were purchased from Apollo Scientific and used as received. All syntheses and sample preparations were performed under anaerobic conditions using a Schlenk line. The preparation and spectral data of the ionic liquids have been described elsewhere [9].

4.2. Synthesis of the copper complexes

4.2.1. [Cu(acac)(bipy)]Cl (**1**)

103 μL (1.0 mmol) of acetylacetone were mixed with 0.1569 g (1.0 mmol) of 2,2′-bipyridine in 10 mL of ethanol. Anhydrous $CuCl_2$ (0.1360 g, 1.00 mmol) dissolved in 25 mL of ethanol were slowly added. The pH was adjusted to 8.5 with 1 M NaOH. The reaction mixture was stirred for 30 minutes at room temperature, after which it was filtered to remove the solid residue. After a week of slow evaporation, dark blue crystals were obtained. Yield: 58.5% (0.445 g). *Anal.* Calc. for $C_{16}H_{18}N_2O_2CuCl{\cdot}1.2H_2O$: C, 50.9; H, 5.0; N, 7.4. Found: C, 50.7; H, 5.1; N, 7.8%. IR (KBr disk, cm^{-1}): 3420 [ν (O–H)], 3043 [ν $(C–H)_{ar}$], 1581 [ν (C=O)] for deprotonated acetylacetone, 1523 [ν (C=C)], 791, wagging mode of coordinated water molecule and 449 [ν (Cu–O)].

4.2.2. [Cu(acac)(phen)]Cl (**2**)

The complex was prepared by the procedure described above, in which bipy was replaced by 1,10-phenanthroline and instead of ethanol, methanol was used. Green crystals were obtained. Yield: 68% (0.322 g). *Anal.* Calc. for $C_{17}H_{15}N_2O_2CuCl{\cdot}2H_2O$: C, 48.6; H, 4.7; N, 6.7. Found: C, 48.4; H, 4.6; N, 6.9%. IR (KBr disk, cm^{-1}): 3450 [ν (O–H)], 3044 [ν $(C–H)_{ar}$], 2988 and 2927 [ν $(C–H)_{alif}$], 1589 [ν (C=O)], 1522 [ν (C=C)], 455 [ν (Cu–O)].

4.3. Instruments

^{1}H NMR spectra were recorded using a Bruker 300 or 400 MHz spectrometer. UV–Vis spectra were recorded using a Perkin–Elmer UV–Visible Lambda 35 spectrophotometer and the temperature was controlled with a Peltier controller from Perkin–Elmer. The EPR spectra were obtained using a Bruker ESP 300E X-band spectrometer, either at 77 K for glassy samples made by freezing solutions in liquid nitrogen or at room temperature. Electrochemical experiments were performed using an EG&G PAR 273A potentiostat/galvanostat controlled by a personal computer.

4.4. Cyclic voltammetry

All experiments were carried in a glass cyclic voltammetry cell purged with nitrogen. Cyclic voltammograms were obtained at room temperature in 0.2 M [^{n}Bu$_4$N][BF_4]/CH_2Cl_2 (or acetonitrile) solution, and in bmimNTf_2 or bmimBF_4 ionic liquids, using a platinum disk working electrode (d = 1 mm). A Luggin capillary connected to a silver wire pseudo-reference electrode was used to control the working electrode potential, and a Pt wire was employed as the counter-electrode. The redox potentials of the complexes were determined using cyclic voltammetry in the presence of ferrocene as the internal standard, and their values are given relative to $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ (FcH/FcH^+) redox couple. We stress that controlled-potential electrolysis to estimate the number of electrons involved in each redox process was not possible due to the fast passivation of the cathode.

Acknowledgments

The authors would like to thank Fundação para a Ciência e Tecnologia for funding through program CIÊNCIA 2007 and projects PTDC/QUI-QUI/098516/2008, PTDC/QUI-QUI/102150/2008 and Pest-OE/QUI/UI0100/2013.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.09.040.

References

[1] T. Welton, Chem. Rev. 99 (1999) 2071.
[2] P. Wasserscheid, C.M. Gordon, C. Hilgers, M.J. Muldoon, I.R. Dunkin, Chem. Commun. (2001) 1700.
[3] M.J. Muldoon, C.M. Gordon, I.R. Dunkin, J. Chem. Soc., Perk Trans. 2 (2001) 433.
[4] R. Lungwitz, M. Friedrich, W. Linert, S. Spange, New J. Chem. 32 (2008) 1493.
[5] J. Bartosik, A.V. Mudring, Phys. Chem. Chem. Phys. 12 (2010) 4005.
[6] S. Pitula, A.V. Mudring, Phys. Chem. Chem. Phys. 12 (2010) 7056.
[7] P.Y. Chen, I.W. Sun, Electrochim. Acta 45 (1999) 441.
[8] I. Persson, Pure Appl. Chem. 58 (1986) 1153.
[9] I. Correia, A. Mota, J.P. Hallett, M.L. Kuznetsov, Phys. Chem. Chem. Phys. 13 (2011) 15094.
[10] L. Becco, A. Rodriguez, M.E. Bravo, M.J. Prieto, L. Ruiz-Azuara, B. Garat, V. Moreno, D. Gambino, J. Inorg. Biochem. 109 (2012) 49.
[11] M. Avelar, A. Martinez, J. Mex. Chem. Soc. 56 (2012) 250.
[12] B.S. Sekhon, Asian J. Pharm. Biol. Res. 1 (2011) 15.
[13] W.L. Hough, R.D. Rogers, Bull. Chem. Soc. Jpn. 80 (2007) 2262.
[14] A. Tovar-Tovar, L. Ruiz-Ramirez, A. Campero, A. Romerosa, R. Moreno-Esparza, M.J. Rosales-Hoz, J. Inorg. Biochem. 98 (2004) 1045.
[15] O.O.E. Onawumi, O.A. Odunola, E. Suresh, P. Paul, Inorg. Chem. Commun. 14 (2011) 1626.
[16] A. Paulovicova, U. El-Ayaan, Y. Fukuda, Inorg. Chim. Acta 321 (2001) 56.
[17] C.C. Su, S.P. Wu, C.Y. Wu, T.Y. Chang, Polyhedron 14 (1995) 267.
[18] O.O.E. Onawumi, O.O.P. Faboya, O.A. Odunola, T.K. Prasad, M.V. Rajasekharan, Polyhedron 27 (2008) 113.
[19] R. Horikoshi, Y. Funasako, T. Yajima, T. Mochida, Y. Kobayashi, H. Kageyama, Polyhedron 50 (2013) 66.
[20] L. Cammarata, S.G. Kazarian, P.A. Salter, T. Welton, Phys. Chem. Chem. Phys. 3 (2001) 5192.
[21] A. Rockenbauer, L. Korecz, Appl. Magn. Reson. 10 (1996) 29.
[22] P. He, H.T. Liu, Z.Y. Li, Y. Liu, X.D. Xu, J.H. Li, Langmuir 20 (2004) 10260.
[23] S. Eugenio, C.M. Rangel, R. Vilar, S. Quaresma, Electrochim. Acta 56 (2011) 10347.
[24] S.S. Moganty, R.E. Baltus, D. Roy, Chem. Phys. Lett. 483 (2009) 90.
[25] L. Xiao, K.E. Johnson, J. Electrochem. Soc. 150 (2003) E307.
[26] L. Yu, H. Sun, J. He, D. Wang, X. Jin, X. Hu, G.Z. Chen, Electrochem. Commun. 9 (2007) 1374.
[27] P.Y. Chen, Y.T. Chang, Electrochim. Acta 75 (2012) 339.
[28] E.P. Grishina, A.M. Pimenova, N.O. Kudryakova, L.M. Ramenskaya, Russ. J. Electrochem. 48 (2012) 1166.
[29] F. Endres, ChemPhysChem 3 (2002) 144.
[30] T.I. Leong, I.W. Sun, M.J. Deng, C.M. Wu, P.Y. Chen, J. Electrochem. Soc. 155 (2008) F55.
[31] H.J. Sun, L.P. Yu, X.B. Jin, X.H. Hu, D.H. Wang, G.Z. Chen, Electrochem. Commun. 7 (2005) 685.
[32] A.B.P. Lever, Inorg. Chem. 30 (1991) 1980.
[33] A.B.P. Lever, Inorg. Chem. 29 (1990) 1271.
[34] http://www.chem.yorku.ca/profs/lever/.