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NEW N^N LIGAND WITH HYDROPHYILIC SUBSTITUENTS FOR COORDINATION COMPLEXES BASED ON M(II) BIOMETAL IONS

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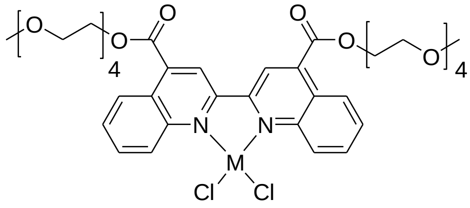
Abstract: *A new N^N chelating ligand based on 2,2'-bisquinoline functionalised with hydrophilic chains and its coordination complexes with Cu(II) and Zn(II) were synthesized and structurally characterized by IR and ^{1}H NMR spectroscopies, atomic absorption spectroscopy and elemental analysis. An accurate photophysical characterisation and conductivity measurements showed the presence of different species in polar solvents solution and in mixtures of solvent/water. The ligand and its Cu(II) and Zn(II) complexes showed no antioxidant activity.*

Keywords: *3d* transition metals; coordination complexes; photophysics; conductivity.

INTRODUCTION

Coordination complexes based on N^N chelating ligands with *3d* transition metals have intricate redox, magnetic and spectroscopic properties controlled by the coordination environment around the metal ion (Pettinari et al. 2010). The ability to tune the above mentioned properties by molecular engineering of the chemical structure allows one to design aesthetically attractive and functionally promising materials. In particular, coordination complexes based on biologically relevant metal ions like Cu(II) and Zn(II) are excellent candidates as metal-based therapeutic (Krajčiová et al. 2014, Starosta et al. 2013, García-Ramos et al. 2013, Liu et al. 2011), antimicrobial (Onawumi et al. 2013, Agwara et al. 2010) or anti-inflammatory agents (Sharma et al. 2009, Odisitse et al. 2007). Moreover, *3d* metal ions may expand the functional roles of inorganic elements applied to biology and make possible studies based on luminescence or magnetic resonance (Haas et al. 2009). However, the insufficient solubility in water of the final complexes can affect the bioavailability of the drugs (Mendiguchia et al. 2013, Jakupec et al. 2008).

The solubility of the coordination complexes, and, hence, their bioavailability may be improved, amongst other, by varying the ligand architecture (Wani et al. 2016). Herein, we report the synthesis and characterization of a new 2,2'-biquinoline ligand (*bq*) substituted in the 4,4'-position with hydrophilic chains of tetraethylene glycol (TEG_2bq). The reaction of the *bq* ligand with Cu(II) and Zn(II) chloride salts afforded the neutral metal coordination complexes with the general formula $[(TEG_2bq)MCl_2]$. The proposed chemical structure of the complexes is presented in Scheme 1.



[(*bq-TEG*)MCl$_2$]

Scheme 1. Proposed chemical structure of complexes $[(TEG_2bq)MCl_2]$, where M = Cu or Zn.

The compounds were characterized by FT-IR and ^{1}H NMR (for the diamagnetic species) spectroscopies, atomic absorption spectroscopy and elemental analysis. Moreover, their photophysical properties in solution and the antioxidant activity of the newly synthesized ligand (TEG_2bq) and its Cu(II) and Zn(II) complexes ($[(TEG_2bq)MCl_2]$) were also investigated.

MATERIALS AND METHODS

Materials and methods

2,2′-biquinoline-4,4′-dicarboxylic acid and tetraethyleneglycol monomethyl ether were purchased from SigmaAldrich; $CuCl_2·2H_2O$ and $ZnCl_2$ were purchased from Merck. All reagents and solvents were of analytical grade and used without further purification. IR spectra were recorded on a Cary 630 FT-IR spectrophotometer, as KBr pellet, in the 400–4000 cm^{-1} range. ^1H NMR spectra were run on a Bruker Fourier 300 MHz spectrometer. To determine the metal content the samples were digested using Digesdahl® Digestion Apparatus Models 23130-20, -21 by HACH (USA). The concentration of copper and zinc ions was then measured using a Flame Atomic Absorption Spectrometer (SensAA, GBC Scientific Equipment, Australia) equipped with a copper/zinc hollow cathode lamp (detection limit: 1-5 μg/mL for copper and 0.4-1.5 μg/mL respectively, integration time 3s). The flame used was an air-acetylene mixture. For each complex, two determinations were made and the average absorbance value was further used. Molar electrical conductivities were measured with a Mettler Toledo FiveEasy plus (FP30) conductivity meter equipped with a Lab conductivity sensor LE740. Melting points were determined on an Olympus BM53X model microscope equipped with a Linkam heating and freezing stage. Absorption spectra were recorded using an Agilent Cary 60 spectrophotometer. Emission spectra were recorded on an UV-Vis Perkin Elmer LS 55 spectrometer. Elemental analyses of products were carried out using a Perkin Elmer 240C-CHN analyzer.

DPPH radical-scavenging activity: The DPPH radical scavenging activity of ligand (*bq*) and complexes ([(*TEG₂bq*)MCl₂]) was performed according to the method of Brand-Williams et al. (Brand-Williams et al. 1995).

Experimental Section

Synthesis of ligand (TEG₂bq)

Di(tetraethyleneglycol) 2,2’-biquinoline-4,4’-dicarboxylate (*TEG₂bq*): A mixture of 2,2′-biquinoline-4,4′-dicarboxylic acid (0.50 g, 1.49 mmol) and thionyl chloride (50 mL) were refluxed under nitrogen until a clear yellow solution was obtained. Excess thionyl chloride was removed and the residue was dried under vacuum for 2 h. The acid chloride was suspended in toluene (30 mL) and treated with a slight excess of tetraethyleneglycol monomethyl ether (0.70 mL, 3.49 mmol). The mixture was heated under reflux for 24 h. The solvent was evaporated before the addition of chloroform (40 mL) and the mixture was washed with a solution of saturated sodium hydrogen carbonate (40 mL), was washed with water (100 mL), dried over anhydrous sodium sulphate, filtered, and evaporated to dryness. The pure product was obtained by column chromatography by using the solvent mixture ethyl acetate/methanol (9:1) as elution medium. Evaporation of the solvent gave a waxy white solid in a 63% yield. M.p. 76-78^{o}C. IR (cm^{-1}, KBr): 3035 ($\nu(CH_3)$), 2876 ($\nu(CH_2)$), 1719 ($\nu(C{=}O)$), 1587 ($\nu(C{=}N)$), 1547, 1501, 1453 ($\nu(C{=}C)$), 1270, 1233, 1189 ($\nu(C{=}O)\text{-}O$), 1152, 1116, 1095 ($\nu_{as}(C\text{-}O\text{-}C)$), 1040 ($\nu_s(C\text{-}O\text{-}C)$). ^1H NMR (300 MHz, $CDCl_3$): δ = 9.33 (s, 2H, $H^{3,3'}$), 8.79 (d, ^3J = 8.5 Hz, 2H, $H^{5,5'}$), 8.32 (d, ^3J = 8.4 Hz, 2H, $H^{8,8'}$), 7.83 (t, ^3J = 8.3 Hz, 2H $H^{7,7'}$), 7.70 (t, ^3J = 8.4 Hz, 2H, $H^{6,6'}$), 4.69 (m, 4H, H^{COOCH2}), 3.98 (m, 4H, H^{CH2O}), 3.85 – 3.45 (overlapped peaks, 24H; $H^{CH2CH2O}$), 3.34 (s, 6H, H^{CH3}). Anal. calcd. for $C_{38}H_{48}N_2O_{12}$ (724.79 $g·mol^{-1}$): C, 62.97; H, 6.68; N, 3.87; found: C, 63.14; H, 6.60; N, 3.99.

General procedure for the synthesis of metal complexes [(*TEG₂bq)*MCl₂]: A solution of ligand (*TEG₂bq*) (0.200 g, 0.276 mmol) in ethanol (20 mL) was added to a solution of metal salts (0.414 mmol) in ethanol (10 mL) and the reaction mixture was stirred for 4 hours at r.t. Then the solvent was evaporated, the residuum dissolved in chloroform, filtrated and recrystallized with hexane.

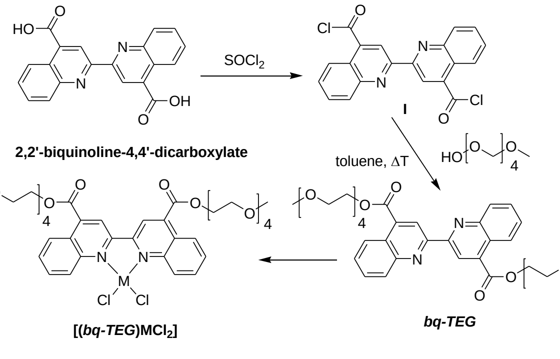
Complex [(*TEG₂bq)*CuCl₂]: brownish waxy solid 79% yield. M. p. 105-107^{o}C. IR (cm^{-1}, KBr): 3035 ($\nu(CH_3)$), 2876 ($\nu(CH_2)$), 1731 ($\nu(C{=}O)$), 1589 ($\nu(C{=}N)$), 1547, 1512, 1457 ($\nu(C{=}C)$), 1261, 1239, 1210 ($\nu(C{=}O)\text{-}O$), 1152, 1116, 1105 ($\nu_{as}(C\text{-}O\text{-}C)$), 1027 ($\nu_s(C\text{-}O\text{-}C)$). Anal. calcd. for $C_{38}H_{48}Cl_2CuN_2O_{12}$ (859.25 $g·mol^{-1}$): C, 53.12; H, 5.63; N, 3.26; found: C, 52.91; H, 6.02; N, 3.19. AAS: Cu % calcd.: 7.24, found: 7.21.

Complex [(*TEG₂bq)*ZnCl₂]: yellowish waxy solid in a 95% yield. M. p. 107-109°C. IR (cm^{-1}, KBr): 3083 (ν (CH$_3$)), 2894 (ν (CH$_2$)), 1733 (ν (C=O)), 1594 (ν (C=N)), 1545, 1513, 1459 (ν (C=C)), 1270, 1243, 1209 (ν (C=O)-O), 1152, 1104, 1095 (ν_{as} (C-O-C)), 1025 (ν_s (C-O-C)). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.11 (s, 2H, H$^{3,3'}$), 8.83 (overlapped peaks, 4H, H$^{5,5'}$, H$^{8,8'}$), 7.09 (t, ^{3}J = 8.3 Hz, 2H H$^{7,7'}$), 7.91 (t, ^{3}J = 8.4 Hz, 2H, H$^{6,6'}$), 4.78 (m, 4H, H^{COOCH2}), 4.02 (m, 4H, H^{CH2O}), 3.85 – 3.45 (overlapped peaks, 24H; H^{CH2CH2O}), 3.31 (s, 6H, H^{CH3}). Anal. calcd. for $C_{38}H_{48}Cl_2N_2O_{12}Zn$ (861.09 g·mol^{-1}): C, 53.00; H, 5.62; N, 3.25; found: C, 52.81; H, 5.83; N, 3.01. AAS: Zn % calcd.: 7.59, found: 7.68.

RESULTS AND DISCUSSIONS

Synthesis and characterization

The ligand (*TEG₂bq*) was prepared adapting a reported method for similar derivatives (Pucci et al. 2011). In particular, the acid chloride of the 2,2'-biquinoline-4,4'-dicarboxylate (**I**) obtained by the reaction with thionyl chloride was coupled with tetraethyleneglycol monomethyl ether (Scheme 2). The pure ligand was obtained by column chromatography and its purity and chemical structure was determined by a combination of IR and ^{1}H NMR spectroscopies and elemental analysis.



Scheme 2. Synthesis of ligand *TEG₂bq* and complexes [(*TEG₂bq*)MCl₂], where M = Cu or Zn.

The synthesis of the complexes was performed according to the literature procedures (Pucci et al., 2012). In particular, the reaction between the ligand (*TEG₂bq*) and small excess of the corresponding metal chlorides in ethanol solution yielded the desired products in relatively high yields. The chemical structure of the complexes is proposed to be a tetracoordination (Figure 1), with one N^N chelating and two chloride ligands completing the coordination sphere of the metal, based on the molecular structure of the complexes having non-substituted biquinoline ligands reported in the literature (Muranishi et al. 2005). The analytical data of complexes [(*TEG₂bq)*MCl₂] (elemental analysis, atomic absorption spectroscopy analysis, IR and ^{1}H NMR spectroscopies - the latter for the diamagnetic Zn(II) complex) are consistent with the proposed structures (experimental section). In particular, the vibrational modes of *bq* ligand show the characteristic upward shifts for the coordinated ligand, with respect to the free molecule (Ozel et al. 2008).

Behavior in solution

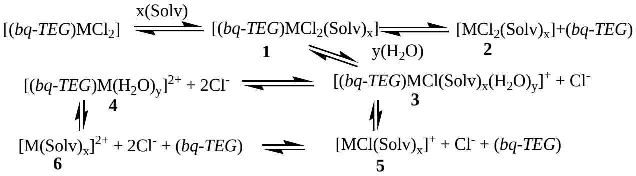
The behavior in solution for the ligand (*TEG₂bq*) and its Cu(II) and Zn(II) complexes was investigated by absorption and fluorescence spectroscopies and conductivity measurements.

The ligand and its Cu(II) and Zn(II) complexes are soluble in polar solvents and insoluble in water and nonpolar solvents. However, the addition of water to the polar solutions does not cause precipitation of the complexes even at high water content (95% volume).

Solutions of Cu(II) complex in different solvents are characterized by different colours: yellow in CH$_2$Cl$_2$, DMF and CH$_3$CN and blue in MeOH and EtOH, suggesting a different coordination environment around the metal centre. Moreover, the yellow colour of the CH$_2$Cl$_2$, DMF and CH$_3$CN solutions of complex [(*TEG₂bq)*CuCl₂] turns blue after addition of water. The solutions of [(*TEG₂bq)*ZnCl₂] are all colourless. After evaporating the solvents, always a brown solid is formed in the case of the Cu(II) complex and a yellow solid in the case of Zn(II) complex, that yield the same physico-chemical analysis data (AAS and elemental analysis) as the pristine [(*TEG₂bq*)MCl₂] complexes.

As documented in literature (Vatsadze et al. 2010), the dissolution of complexes of this type can occur in several steps, following different equilibrium reactions triggered by the competition of the coordinating solvent with the bidentate ligand (Scheme 3).

In particular, after the dissolution of the complex, a change of the geometry may be induced by coordinating solvents yielding penta- or hexacoordinated species (**1**, **3** and **4** in Scheme 3). Strong donor solvents may induce in steps the complete dissociation of the complex to form solvated metal chlorides (**2**, **5** and **6** in Scheme 3), as evidenced by spectrophotometric studies and ESI-mass spectrometric measurements (Vatsadze et al. 2010).



Scheme 3. Chemical species that may occur at the dissolution of complexes [(*TEG*$_2$*bq)*MCl$_2$] in different solvents (Solv).

Photophysical properties

In the absorption spectra of *TEG*$_2$*bq* recorded at room temperature in ethanol solution (Figure 1), two bands are detected (279 nm (ε = 31500 $M^{-1}\cdot cm^{-1}$) and 340 nm (ε = 15550 $M^{-1}\cdot cm^{-1}$)) originating from $\pi-\pi^*$ transitions on the aromatic rings of the 2,2'-biquinoline (Pucci et al., 2011). The absorption spectrum of the ligand does not change with varying the solvent. The ligand emits at 420 nm in the violet region. In Figure 1 the normalized absorption and emission spectra of the ligand in ethanol solution are presented.

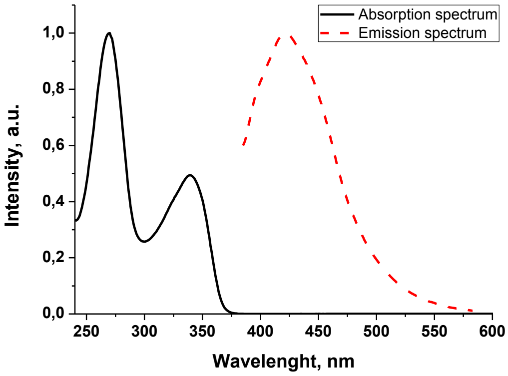


Figure 1. Absorption and emission spectra of ligand *TEG*$_2$*bq* in EtOH solution.

The UV-Vis data of complexes [(*TEG*$_2$*bq)*MCl$_2$] recorded in different solvents is summarized in Table 1.

Table 1. UV-Vis data for solutions of complexes [(*TEG*$_2$*bq)*MCl$_2$] in different solvents

Solvent	λ_{max}/nm (ε/$M^{-1}\cdot cm^{-1}$)	
	[(*TEG*$_2$*bq)*CuCl$_2$	[(*TEG*$_2$*bq)*ZnCl$_2$
CH_2Cl_2	278 (56950)	277 (46300)
	305 (11100)	310 (5800)
	376 (23070)	318 (5900)
	444 (1650)	371 (19050)
		380 (21550)
CH_3CN	272 (47080)	229 (26550)
	324 (13450)	272 (54400)
	347 (15730)	319 (10750)
	366 (12250)	357 (16050)
	445 (850)	377 (17000)
DMF	340 (23800)	340 (21850)
EtOH	272 (44400)	270 (41050)
	343 (18950)	340 (21250)
	368 (8850)	
	578 (1350)	
MeOH	270 (46050)	268 (40750)
	339 (21500)	340 (20450)
	576 (2450)	

In particular, the spectra in DMF of the Cu(II) complex is similar to that of the ligand, showing a hyperchromic effect only, whereas in CH_2Cl_2 and CH_3CN solution the lower energy $\pi-\pi^*$ transition is red shifted and a new band centred at 445 nm appears (Figure 2 up). The latter may be attributed to charge transfer transitions of tetrahedral Cu(II) complexes (Lever, 1968). Moreover, in MeOH and EtOH solutions transition bands centred at around 577 nm (Figure 2 down) suggest a change in the coordination environment around the metal centre.

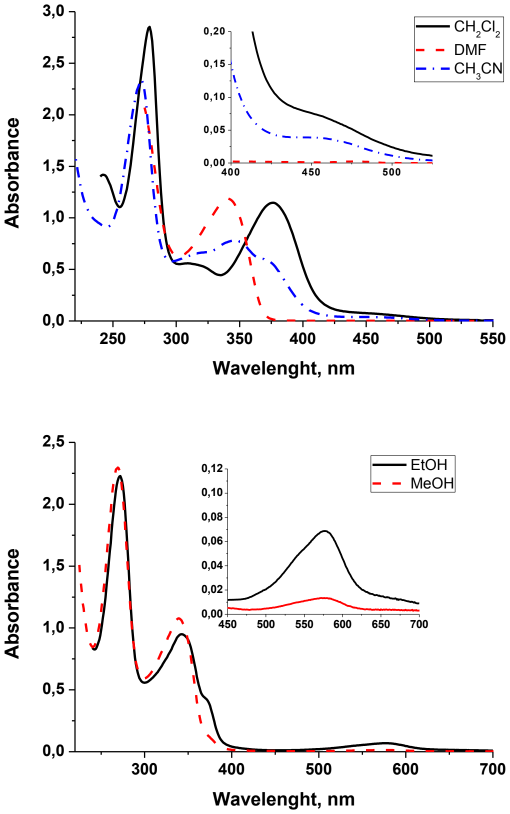


Figure 2. Absorption spectra of complex [(*TEG₂bq*)$CuCl_2$] in CH_2Cl_2, DMF and CH_3CN (up) and EtOH and MeOH (down) solutions.

In solvent/water mixture 5:95 volume, the absorption spectra of the [(*TEG₂bq*)$CuCl_2$] complex show similar features with the spectra of the ligand (Figure 3), but in all cases, a weak transition centred at 580 nm reveal the presence of octahedral species (Ozutsumi et al. 1991).

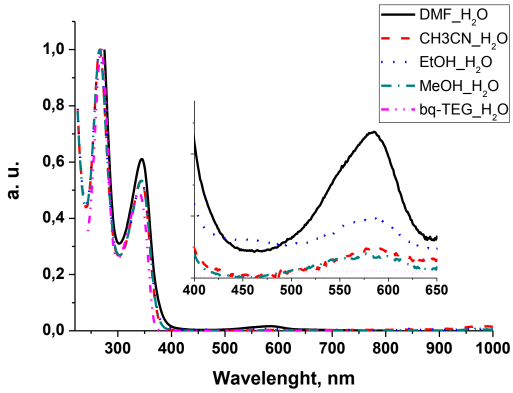


Figure 3. Absorption spectra of complex [(*TEG₂bq*)$CuCl_2$] in mixture of CH_2Cl_2, DMF, CH_3CN, EtOH and MeOH / water 5:95% volume solutions.

Regarding the Zn(II) complex, their spectra in solvents are similar with the spectra of the Cu(II) complexes, however lacking of the charge transfer bands (Figure 4).

In a mixture of solvent/water 5:95 volume, the absorption spectra of complex [(*TEG₂bq*)$ZnCl_2$] is similar with the absorption spectra of the ligand with small bathochromic or hypsochromic shifts.

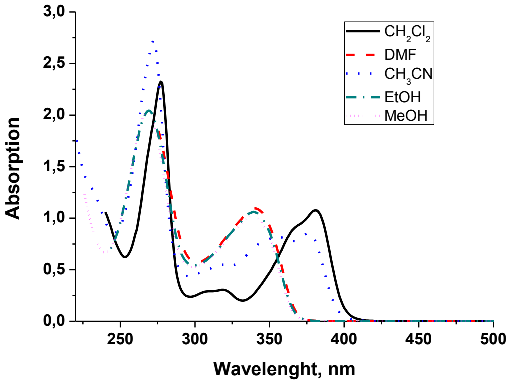


Figure 4. Absorption spectra of complex [(*TEG₂bq*)$ZnCl_2$] in CH_2Cl_2, DMF, CH_3CN, EtOH and MeOH solutions.

Regarding fluorescence, complex Zn(II) does not emit in all solvents, but in solvent/water mixture have similar emission as the ligand *TEG₂bq* with small blue shifts in CH_3CN and EtOH and red shift in MeOH (Figure 5). The change in the fluorescence spectra of Zn(II) complexes based on 2,2'-biquinoline ligand is due mainly to the conformational change of *TEG₂bq* ligand (Yagi et al. 1994).

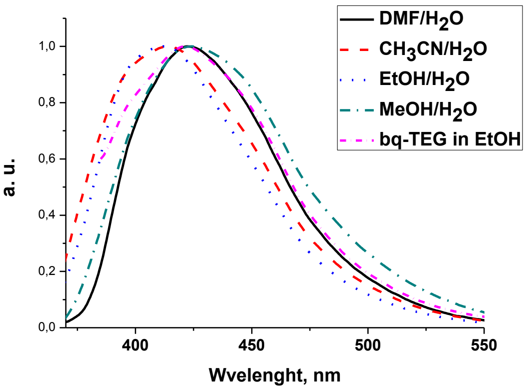


Figure 5. Emission spectra of complex [(*TEG₂bq*)$ZnCl_2$] in mixture of solvent/water, where solvent is CH_2Cl_2, DMF, CH_3CN, EtOH and MeOH.

Conductivity measurements

Conductivity measurements performed at a concentration of 10^{-3} mol·L^{-1} showed a neutral character in most of solvents, except for [(*TEG₂bq)*CuCl₂] in MeOH, where a value of 83 Ω^{-1}·mol^{-1}·cm^{2} reveal the presence of a monovalent specie (Geary, 1971). The results are presented in Table 2.

Table 2. Conductivity data for complexes [(*TEG₂bq)*MCl₂] in different solvents

Solvent	Conductivity (Ω^{-1}·mol^{-1}·cm^{2})	
	[(*TEG₂bq)*CuCl₂]	[(*TEG₂bq)*ZnCl₂]
CH_2Cl_2	< 10	< 10
DMF	34	< 10
CH_3CN	< 10	< 10
EtOH	< 10	< 10
MeOH	82	41

However, with the addition of water, monovalent or even bivalent species are formed, as showed in Figures 6 and 7.

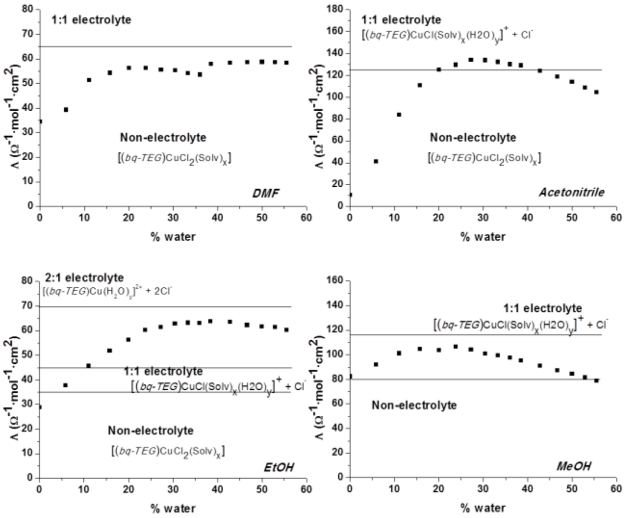


Figure 6. Conductivity measurements of complex [(*TEG₂bq)*CuCl₂] in mixture of solvent/water.

Based on the differences existent in the absorption spectra for complex [(*TEG₂bq)*CuCl₂] and in the emission spectra of complex [(*TEG₂bq)*ZnCl₂] in mixtures of solvent/water with respect to the absorption and emission spectra of the ligand, the monovalent and bivalent species are proposed to be the solvated species **3** and **4** from Scheme 3, probably in equilibrium with the solvated metal chlorides **5** and **6**.

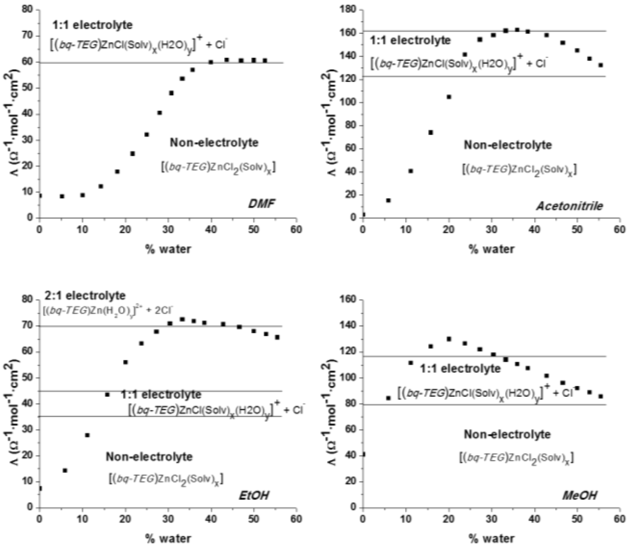


Figure 7. Conductivity measurements of complex [(*TEG₂bq)*ZnCl₂] in mixture of solvent/water.

Antioxidant activity

The antioxidant activity of the ligand *TEG₂bq* and its Cu(II) and Zn(II) complexes was tested using 1,1-diphenyl-2-picrylhydrazyl (DPPH) in ethanolic solution, according to the Brand-Williams method (Brand-Williams et al. 1995). However, no scavenging effect was evidenced for neither of compounds.

CONCLUSIONS

In search of highly soluble coordination complexes based on biometals for biological applications, we have prepared and characterized a new N^N donor ligand functionalized with hydrophilic chains. Its Cu(II) and Zn(II) complexes are highly soluble in polar solvents. The complexes are tetrahedral, with a chelating N^N ligand and two monodentate chlorine ligands completing their coordination sphere.

However, as demonstrated by an accurate photophysical investigation and conductivity measurements, in solution different species co-exist, depending on the coordinating strength of the solvent. Solutions of CH_2Cl_2, DMF and CH_3CN contains only neutral tetrahedral [(*TEG₂bq)*MCl₂] whereas in alcohols neutral octahedral species are present, formed by coordinating solvents. By addition of water to the polar solvents, ionic species are formed, the solvent displacing the chlorine ligands and/or the chelating N^N ligand.

Although the complexes did not show antioxidant activities in ethanolic solution, their use in the biological related fields may be relevant as carriers of active ligands, 2,2’-biquinoline being a well-known 1,4-diimine-type ligand, from the quinoline class, which are known to possess biological properties, such as antimicrobial, anti-inflammatory, etc. (Ingle et al. 2012).

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