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Synthesis and full characterization of new symmetric bis-triazol ligand and complexes with divalent Nickel, Copper and Zinc

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Absract

The synthesisvia the Cu(I)-catalyzed Huisgen dipolar cycloaddition *of N,N*'-Bis(triazolyl) *N,N*-dimethyl-propyldiamine**L**^{2}, from commercial *N,N'*-dimethyl-propyldiamine. This ligand bears two propanol moieties connected to triazoles via the azote for increasing water solubility and overcome the dissolution problems encountered in the previous works. The interaction of these ligands with NiII, CuII, and ZnII cations were fully investigated by UV/Vis and ^{1}H and ^{13}C NMR, cyclic voltammetry and electron paramagnetic resonance (EPR) spectroscopies. The copper(II) complex have a square-based pyramidal geometry, as witnessed by the reported spectroscopic, UV/Vis and EPR features. The stoichiometry of the complexes was established from the elemental analysis, Mass and UV-visible spectroscopies.

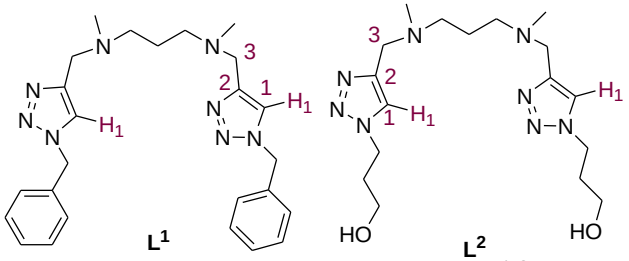
Keywords: N,N-diamine; [1,2,3]Triazole; Cu^{II} complexes; Cyclic voltammetry.

1. Introduction

Organocomplexes of transition metals achieved a great interest because of their potential roles as biological models, catalysts for organic reactions, and as structural components for the synthesis of new metal-supramolecular structures [1-5]. A large array ligands for metal transition coordination has been synthesized [1-7]. Ligands containing triazole rings have attracted interest as versatile ligands with a variety of coordination modes with transition metal centers, because of the versatile chemistry f triazoles and their various donor sites or for acting as bridging ligands for copper and some other rare transition metal coordination too [8] . A large array ligands incorporating triazoles has been synthesized the last decay [9-11]. In addition, triazole derivatives display a broad range of biological activity, finding application as antimicrobial, antifungal, anticonvulsants, antiviral and antitumor agents [12-15].

Recently, we published the synthesis of ligands bearing triazoles using the Cu(I)-catalyzed version of the [3+2] Huisgen azide–alkyne cycloaddition with good complexing properties towards copper, with the aim of obtaining models of copper enzymes [16-18] . The complex based on **L**^{3} was the first solid-state structural study of a copper complex that involved coordinated diaza[18]crown-6 and 1,2,3-triazolyl ligands [16] . We have shown that the ligands based diaza[18]crown-6 and diaza[15]crown-5 ethers are a versatile receptors that can adapt to the coordination sphere to the particular metal cation[18]. Whereas *N,N*-dimethylethylamine based complexes adopt pyramidal geometry [17] . All these complexes showed promising catalytic activity in the oxidation of DTBC (catechol) to DTBQ (quinone) but the solubilization in water have not led to sufficiently concentrated solution of the complexes.

We reported herein the extension of our previous studies based on the 'click' synthesis towards the synthesis of new tetradentate acyclic ligand (L^{2}) from a N,N′-dimethyl-1,2-diaminopropane bearing propanol arms to increase water solubility of the formed complexes [16-18]. The syntheses were performed using the Cu(I)-catalyzed version of the Huisgen reaction. The M(II)-complexes (M = Cu, Ni, and Zn) of this ligand were isolated (as their perchlorate salts) and characterized by different techniques: elemental analysis, FT-IR, UV-visible and EPR spectroscopies, HRMS+, and cyclic voltammetry.



Scheme 1: *structures of Ligands* ***L*** *[1–2]*.

2. Experimental section

2.1. Materials

Chemicals and solvents (reagent grade or better) were purchased from Sigma-Aldrich except spectrophotometric-grade DMF which was purchased from Alfa-Aesar [ref. 13808]. Anhydrous solvents were dried by usual procedures and stored over 4Å molecular sieves under Ar before use. Chromatography was carried out using Grace silicagel (Davisils LC60A 70–200 mm) or basic Al_2O_3 when stated (Sigma-Aldrich ref. 199443). ^1H & ^{13}C-NMR spectra were recorded on a DRX400 spectrometer operating at 400.13 MHz for ^1H and 100.61 MHz for ^{13}C or and Bruker AC 250 FT (250 MHz for proton, 62.5 MHz for carbon) spectrometers in CD_3CN and D_2O if no other conditions are stated. CHN elemental analyses were performed using a Thermo Finnigan EA 1112 Series Flash Elemental Analyzer.

ES+-HRMS spectra were obtained using a Bruker microTOFQ mass spectrometer with capillary tensions between -1200 and -4500 V from diluted MeCN solutions. FT-IR spectra were obtained from KBr-pellets (if not other stated) on a Perkin Elmer Spectrum 1000 spectrophotometer. UV-visible spectra were recorded on a Perkin-Elmer Lambda1050 UV Vis-NIR spectrophotometer using a 1 cm optical path length cell at T = 298 K. Cyclic voltammetry (CV) was performed using a Radiometer PST006 potentiostat using a conventional three-electrode cell at rt. The KCl calomel electrode (SCE) was separated from the test compartment using a bridge tube. The test solution was dimethylformamide containing 10^{-1}M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The working electrode was a 10 mm Pt wire and the counter-electrode a 1 cm^2 vitreous carbon disc. 5.0 -10^{-4} M fresh solution of each studied compound was used and purged for 5 min with Ar before each measurement. All potentials were quoted versus SCE. Under these conditions the redox potential of the couple Fc+/Fc was found to be 0.47 V. EPR spectra were recorded using a continuous-wave EMXplus spectrometer (Bruker Biospin GmbH, Germany) equipped with a high sensitivity resonator (4119HSW1, Bruker). The spectrometer was tuned such that settings (modulation coils, incident microwave power) were not distorting the EPR signal (X-band Larmor frequency B9.3 GHz and Q-band Larmor frequencyB34 GHz). Measurements were carried out in frozen 10^{-3}M DMF (ACS reagent Z 99.8% GC) solutions of copper(II) complexes held at 100 K with liquid nitrogen.

2.2. Synthesis

General procedure I: One-pot synthesis of ligand L^2.

To symmetric sec. N,N'-dimethylpropyldiamine (17.02 mmol) in 10 mL acteonitrile/water (1:1, v/v) was added triethylamine (40 mmol) and propargyl bromide (4.05 g, 34.04 mmol). After stirring at rt for 2 h, propanolazide (34.04 mmol), sodium ascorbate (6 mmol) and $CuSO_4$ (2 mmol) were added to the reaction mixture, and was stirred at room temperature over night. The reaction mixture was concentrated in vacuum to give a crude oil residue. The pure products were purified by liquid chromatography (LC) on silica or alumina with mixtures of CH_2Cl_2–MeOH as eluents.

General procedure II:

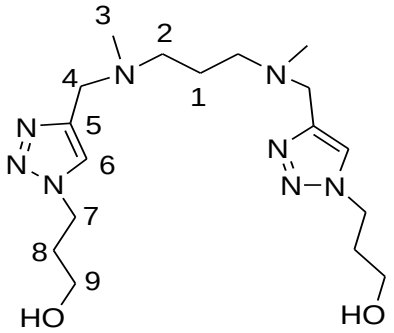
Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great care!

$M(ClO_4)_2\_6H_2O$ (M, Cu, Ni, Zn) (1.2 equiv.) was dissolved in a solution of the ligand (1.2 equiv.) in " mL of a mixture of acetonitrile–water–Ethanol (1:1:1, v/v/v) at room temperature. The resulting suspension was stirred at 70 °C for 2 h, allowed to cool to room temperature, filtered through a small cotton pad, concentrated to half, diluted with two drops of DMF (ca. 30 mg), and finally stored for several days in the dark at 41°C.

Ligand ***L*** ^{1}.As described in the general procedure I (80% yield).
^{1}HNMR(250 MHz, CD_3CN): δ ppm 7.68 (s, 2H, $H_{triazol}$), 7.26–7.45 (m, 10H, H_{arom}), 5.53 (s, 4H, CH_2Ph), 3.59 (s, 4H, CH_2-Triazol), 2.33 (t, J = 4.5Hz, 4H, NCH_2), 2.15 (s, 6H, CH_3), 1.96 (m, 2H, $NCH_2\underline{CH_2}$). ^{13}C NMR (62.5 MHz, CD_3CN): δ ppm 145.3(C5), 136.6(C8), 129.3(C9), 128.6(C11), 128.3(C10), 123.7(C6), 54.7(C2), 53.7(C7), 52.2(C4), 41.7(C3), 25.2(C1).
HRMS: calcd. for $C_{25}H_{32}N_8$ $[M + H]^+$445.2750, found 445.2759
Mp : 83-85°C

$[NiL^1]^{2+}$, $2ClO_4^-$, light green oil, 90%
HRMS: calcd. for$[C_{25}H_{32}ClNiN_8O_4, ClO_4]^+$ 601.16, found 601.15 . Anal.calcd. for$[C_{25}H_{32}ClNiN_8O_4, 2ClO_4]$, CH_3CN, H_2O: C, 42.3; H, 4.8; N, 16.4. found: C, 42.2; H, 4.6; N, 15.8.

$[ZnL^1]^{2+}$, $2ClO_4^-$, white yellowish oil, 90%
^{1}HNMR(250 MHz, CD_3CN): δ ppm 8.0 (s, 1H, $H_{triazol}$), 7.99 (s, 1H, $H_{triazol}$), 7.36–7.48 (m, 10H, H_{arom}), 5.69 (s, 2H, CH_2Ph), 5.68 (s, 2H, CH_2Ph), 4.15-3.72 (dd, 2H, J = 9.8Hz, H_4), 4.07-3.82 (dd, 2H, J =9.8Hz, H_4), 3.20–3.08 (m, 2H, H_2), 2.99–2.87 (m, 2H, H_2), 2.46 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 1.96 (m,2H, $NCH_2\underline{CH_2}$). ^{13}C NMR (62.5 MHz, CD_3CN): δ ppm 143.5(C5), 143.3(C5), 134.8(C8), 129.4(C9), 128.9(C11), 128.6(C10), 124.3(C6), 62.1(C2), 59.9(C2), 55.4(C4), 54.3(C7), 53.0(C4), 45.5(C3), 44.7(C3), 22.0(C1), 21.9(C1). HRMS: calcd. for$[C_{25}H_{32}ClZnN_8O_4, ClO_4]^+$ 607.16, found 607.15 . Anal.calcd. for$[C_{25}H_{32}ClZnN_8O_4, 2ClO_4]$, CH_3CN, H_2O: C, 42.3; H, 4.8; N, 16.4. found: C, 42.2; H, 4.6; N, 15.8.



Ligand ***L*** ^{2}.As described in the general procedure II (75% yield).
^{1}H NMR(250 MHz, D_2O): δ ppm 7.96 (s, 2H, H-triazol), 4.47 (t, J = 6Hz, 4H, H-9), 3.82 (s, 4H, CH_2-Triazol), 3.51 (t, J =6.0Hz, 4H, H-7), 2.50 (m, 4H, H-2), 2.28 (s, 6H, H-3), 2.07 (t, J =6.0Hz, 4H, H-8), 1.84 (m, 2H, H-1). ^{13}C NMR (62.5 MHz, D_2O): δ ppm 141.4(C5), 125.7(C6), 58.2(C9), 53.6(C2), 49.9(C4), 47.6(C7), 40.5(C3), 31.8(C8), 22.3(C1). HRMS: calcd. for $C_{17}H_{32}N_8O_2$ $[M + H]^+$ 381.2721, found 381.2707.

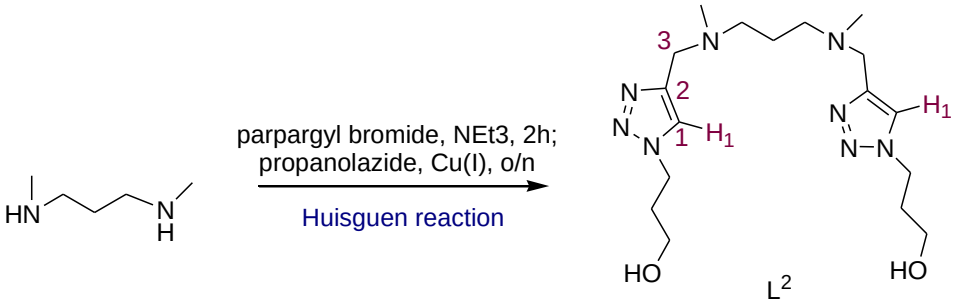
$[CuL^2]^{2+}$, $2ClO_4^-$, dark blue oil, 96%.
HRMS: calcd. for $[C_{17}H_{32}N_8O_2Cu, ClO_4]^+$542.1424, found 542.1452 .
IR (KBr, cm^{-1}): ν= 3121, 2950(ν_{C-H}), 1637, 1466, 1397, 1092(ν_{ClO4-}), 1068, 941, 804, 626.
$\lambda_{max}(\varepsilon)$ = 567 nm (311 $M^{-1}cm^{-1}$)
EPR (DMF): $g^{\perp}$= 2.060, g// =2.240, $A^{\perp}$ = 0.0012cm^{-1}, A// = 0.018cm^{-1}.

$[NiL^2]^{2+}$, $2ClO_4^-$, green oil, 90%
HRMS: calcd. for$[C_{17}H_{32}N_8O_2Ni, ClO_4]^+$ 537.1481, found 537.1486 .
IR (KBr, cm^{-1}): ν= 3392, 2930(ν_{C-H}), 1654, 1437, 1383, 1253, 1149, 1110, 1083(ν_{ClO4-}), 940, 804, 689, 637, 626.
$\lambda_{max}(\varepsilon)$= 250 nm (130 $M^{-1}cm^{-1}$);383 nm (32 $M^{-1}cm^{-1}$);741 nm (6 $M^{-1}cm^{-1}$)
$[ZnL^2]^{2+}$, $2ClO_4^-$, yellowish white oil, 95%.
^{1}HNMR(250 MHz, CD_3CN): δ ppm 8.17 (s, 2H, H6), 4.55-4.49 (m, 4H, H9), 3.55 (t, 4H, *J* = 5.8Hz, H7), 3.25-3.21 (dd, 2H, *J* =7.5Hz, H4), 3.19-3.14 (dd, 2H, *J* =7.5Hz, H4'), 3.13-2.00 (m, 4H, H2), 2.75-2.67 (m, 3H, H3), 2.15-2.05 (m, 6H, H1 and H8), 2.00-1.89 (m, 3H, H3'). ^{13}C NMR (90 MHz, CD_3CN): δ ppm 136.0, 134.0, 133.6, 128.3, 127.5, 126.5, 66.3, 66.2, 57.8, 51.7, 51.2, 49.7, 48.9, 46.7, 44.9, 39.1, 31.9, 30.8, 30.3, 28.2, 21.8, 21.4, 20.2.
HRMS: calcd. For$[C_{17}H_{32}N_8O_2Zn, ClO_4]^+$ 543.1419, found 543.1419 .
IR (KBr, cm^{-1}): ν= 3448, 2929, 1648, 1617, 1560, 1466, 1235, 1141, 1091(ν_{ClO4-}), 940, 803, 669, 627.
$\lambda_{max}(\varepsilon)$= 206 nm (20400 $M^{-1}cm^{-1}$)

3. Results and Discussions :

3.1. Synthesis and characterisation of L^2

Acyclic ligand **L^2** was isolated in fair to good yield using a slight modification of the one-pot method reported by Yan et al.[19] from commercial secondary bis-N-methyl amine propyl (i.e scheme 2 and general procedure I).The ligand was purified twice by silica and/or neutral alumina chromatography to give satisfactory yields (75%).



Scheme 2: One-pot synthesis of L^2 via the Cu(I)-catalyzed Huisgen reaction.

The ligand structure was unambiguously ascertained by ^{1}H & ^{13}C-NMR, FT-IR, and ES^+-HRMS. ^{1}H NMR spectra of this ligand exhibit the expected time-averaged 2-fold symmetry and the characteristic aromatic singlet between 7.5 and 8.0 ppm for the two isochronous triazol protons at the NMR time scale (CD_3CN, 298 K).Further information about the isolation and full characterization of ligand **L^2** is provided in the experimental section.

3.2. Transition Metals (II) Complex synthesis

Transition metals M(II) complexes were isolated from **L^2** and $M(ClO_4)_2$ hexahydrate (M = Cu, Ni, Zn) in the presence of acetonitrile and dimethylformamide (traces) in fair to excellent yield within a week. The stoichiometry 1 : 1 / L : Cu(II) of the complex was established from the elemental analyses and UV-visible spectroscopy. Mononuclear nature of complexes is confirmed by the mass spectrum, the results are consistent with the theoretical values calculated on the basis of the isotopic distribution of the atoms of all complexes. In IR spectrum, non-ligand peak at 345–365 (480-495) cm^{-1} of complexes were assigned to ν(M-N) stretching vibrations. In addition the IR spectra of the complex showed a strong band in the region 1088-1092 cm^{-1} ascribable to the counter anion ClO_4^-.

3.2.1. EPR and Electronic Spectroscopies

The UV/Vis spectrum of a solution of **L^2** and complexes are recorded in acetonitrile at 298 K. In UV/Vis spectra of **L^2**, we observe the increase of the band d-d absorption upon addition of aliquots of a $M(ClO_4)_2$; in the case of Zn^{2+}, the intensity of the shoulder at 206 nm decreases, until stabilization at M/L = 1 (see Figure.2), indicating a 1:1 metal–ligand stoichiometry. The same for variation of the LMCT and the d-d absorption upon addition of $M(ClO_4)_2$ solution (see Figure 1 & Figure 2)

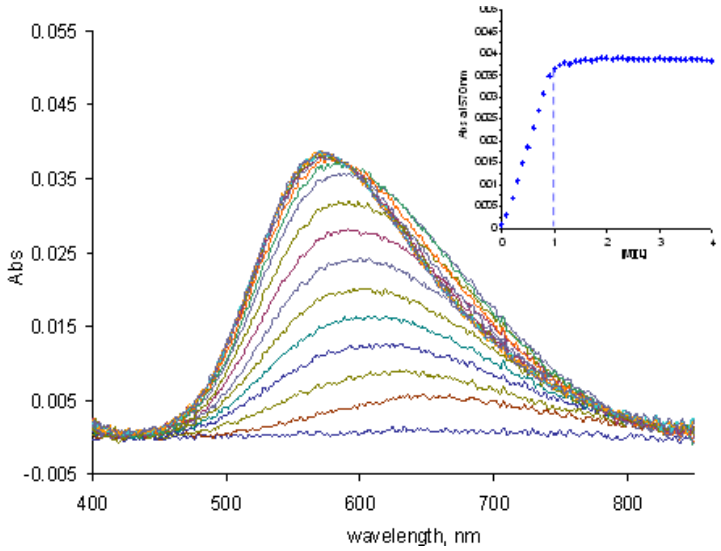


Figure 1: UV-visible spectral changes of $\mathbf{L^2}$ upon addition of aliquots of a solution of $Cu(ClO_4)_2$ in CH_3CN at 298 K.

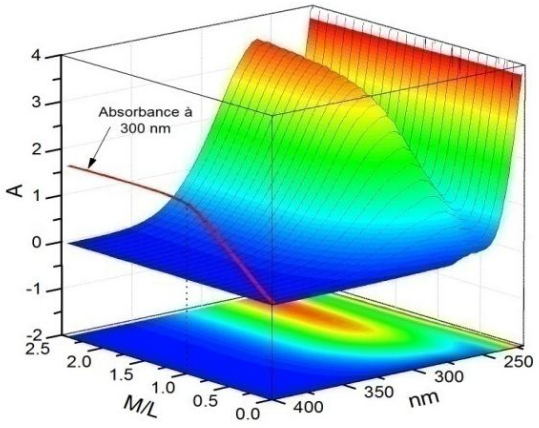


Figure 2: Variation in UV/Vis spectra of $\mathbf{L^1}$ upon addition of aliquots of a $Cu(ClO_4)_2$ solution (10 µL, 0.0101 m) in acetonitrile.

The UV/Vis spectrum of a solution of $[Cu(\mathbf{L^2})]^{2+}$recorded in acetonitrile at 298 K shows a intense d–d band at at 567 nm (ε= 311 $m^{-1}cm^{-1}$). [24] This transition at 567 nm is consistent with the transition expected for a copper (II) complex of square pyramid geometry, [25] and assigned to d-d transitions $dz^2 \rightarrow dx^2\text{-}y^2$, $dxy \rightarrow dx^2\text{–}y^2$. [26] The order of d orbitals in a PCB field being $dx^2\text{-}y^2 > dz^2 > dxy > dxz, dyz$.

In order to confirm the various coordination environments of copper(II) complexes, EPR spectroscopic criteria have been developed, taking into account the kind of the donor atoms involved in the copper(II) coordination sphere. Indeed, EPR spectroscopy of the complex $[Cu\mathbf{L^2}(MeCN)]^{2+}$recorded at 100 K in frozen DMF and presented in (Figure 3), displayed spectrum with $g_{//}$ = 2.24, $g_{\perp}$ = 2.06.$g_{//} > g_{\perp} > 2.0023$ indicating square pyramidal geometry for Cu(II) with the $dx^2\text{-}y^2$ ground state and characteristic of a Cu(II)-ion coordinated with four N-nuclei within a planar (or near planar) configuration as reflected by the g‖/A‖ ratio given as a rough estimate of coordination geometry, [27-28] and rules out the possibility of a trigonal bipyramidal structure for which $g_{\perp} > g_{//}$ = 2.0023 is expected. [27-28] Indeed, Values of 110–120 are reported as typical of 'planar' complexes while the range between 130–150 is characteristic of slight to moderate distortion and 180–250 indicates strong distortion [28].

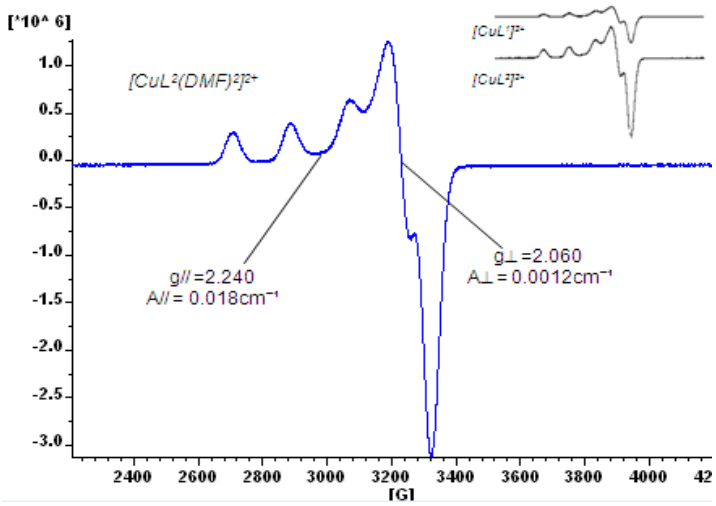


Figure 3: EPR spectra of copper(II) complexes of $[Cu\mathbf{L}^{1}(MeCN)]^{2+}$, $[Cu\mathbf{L}^{2}]^{2+}$ recorded at the X-band (10^{-3} M in DMF at 100 K).

The $g_{//}$ value provides information regarding the nature of metal-ligand bond. [29] The value $g_{//}$ is normally 2.3 or larger for ionic and less than 2.3 for covalent metal-ligand bonds. The $g_{//}$value obtained indicates a significant degree of covalency in the metal-ligand bonds.
EPR data for the $[Cu\mathbf{L}^{2}]^{2+}$complex are summarized in Table 2.

Table 2: EPR-spectral data of $[Cu\mathbf{L}^{2}]^{2+}$ (10^{-3} M in DMF at 100 K).

	g Tensor		Hyperfine coupling tensor to ^{63}Cu		
Complex	$g_{\perp}$	$g_{\parallel}$	$A(Cu)_{\perp}10^{-4}cm^{-1}$	$A(Cu)_{\parallel}$ $10^{-4}cm^{-1}$	$g_{\parallel}$/ $A(Cu)_{\parallel}$
$[CuL^{2}(MeCN)]^{2+}$	2.060	2.240	12	180	124

The electronic spectrum of $[Ni(\mathbf{L}^{2})]^{2+}$in the UV-visible region (200-800 nm) exhibits two bands at 590 nm and 383 nm , indicating the five-coordinated square-pyramidal coordination geometry of the Ni(II) atom in the complex. The two bands are assigned to the d-d transitions of the Ni(II) ion. The lower energy band at 590 nm is considered to be due to $^{3}A_{2g}\rightarrow{}^{3}T_{1g}(F)$ and the higher energy band at 370 nm is due to the $^{3}A_{2g}\rightarrow{}^{3}T_{1g}(P)$ transition of Ni(II) in the square-environment. The same for the $[Ni(\mathbf{L}^{1})]^{2+}$ complex.
The spectrum of $[Zn(\mathbf{L}^{1})]^{2+}$ and $[Zn(\mathbf{L}^{2})]^{2+}$ shows one shoulder at 206 nm with ε = 20400M^{-1} cm^{-1} attributed to the π–π* transition of ligands.

3.2.2. Electrochemical study: Cyclicvoltammograms

The electrochemical behavior was studied starting potential at +0.2 V towards negative values and keeping the potential range between - 0.4 and +0.8 V to avoid the irreversible formation of Cu^{0} and the oxidation of the solvent throughout the study, because It is noteworthy that the formation of Cu^{0}-species occurs at about -1.5 V as an irreversible process and that the formation of a Cu(III)-complex was not detected before the solvent oxidation which started at +1.5 V under our experimental conditions.
The Figure 4 displays the electrochemical behavior of $[Cu\mathbf{L}^{2}](ClO_{4})$ and Table.2 summarizes the electrochemical results corresponding to the first cathodic peak (1st scan towards negative potential at three increasing scan rates) which was assigned to the reduction of the initial and stable geometric form, i.e. Cu(II)st to Cu(I) and the electrochemical data for the anodic peak assigned to the oxidation of Cu(I) to Cu(II): Epc (mV vs. SCE) and Ipc (µA) in Cu(II)-complexes from $\mathbf{L}^{2}$ ligand at three different scan rates. First cathodic peak reduction potential (i.e. Epc) analyses revealed the ligand-based electrochemical behavior of the complex.

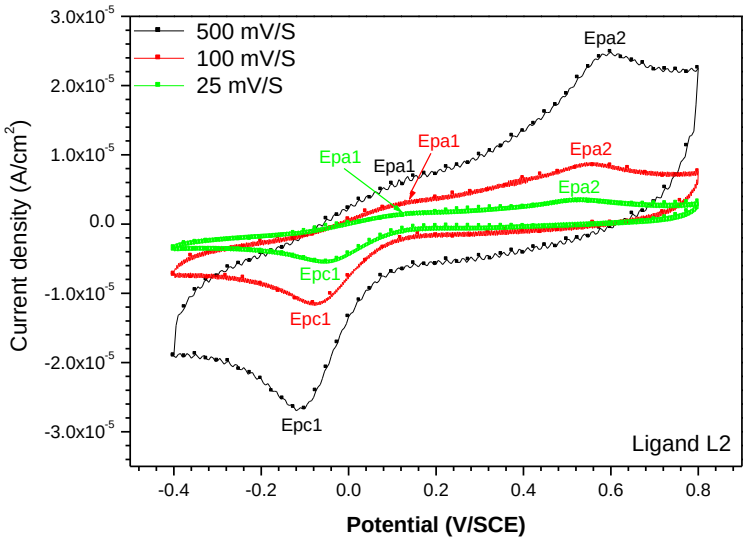


Figure 4: Cyclic voltammograms of 5×10^{-4} M solution of $[Cu\mathbf{L}^2]^{2+}$(left) in 0.1 M Bu_4NPF_6 in DMF at three different scan rates. Reference electrode: SCE; working electrode: Pt (0.08 cm^2).

A reductive-controlled potential coulometry realized below the 1st cathodic peak at -0.4 V showed that the total quantity of electricity exchanged corresponds to one electron per mole of the copper complexes.

Table 2: Electrochemical data for the cathodic and the anodic peaks assigned respectively to the reduction of Cu(II) to Cu(I): Epc (mV vs. SCE), Ipc (µA) and the oxidation of Cu(I) to Cu(II): Epc (mV vs. SCE), Ipc (µA) in Cu(II)-complexes from $\mathbf{L}^2$ at three different scan rates.

	Cathodic peaks			Anodic peaks		
Scan rate	Epc1	Ipc1	Epa1	Ipa1	Epa2	Ipa2
25 mV/s	-50.22	-5.39	0.15	1.53	0.52	3.54
100 mV/s	-75.96	-11.5	0.15	3.18	0.55	8.65
500 mV/s	-114.95	-26.4	0.12	6.18	0.59	24.5

The electrochemical data illustrated that the 1st reduction peak potential of the complex, i.e. Epc1, depends on the scan rate since its value increases as the scan rate decreases. For each scan rate, the CVs in the positive part display two re-oxidation waves. The 1st wave, i.e. Epa1 at a potential of about 85 mV vs. SCE, was attributed to the re-oxidation of Cu(I)st to Cu(II)met1. The other waves, corresponding to Epa2, was ascribed to the re-oxidation of metastable Cu(I)met1 and Cu(I)met2 species formed by the reduction of Cu(II)st during the 1st scan. However, reversing the scan direction at 800 mV induces only one reduction peak which was clearly observed (i.e. Epc1). One should notice that this system can be almost totally reversed at all scan rates.

3.2.3. NMR Investigations of the Zinc complexes

The ^1H and ^{13}C spectra of the Zn(II) compound were recorded in CD_3CN solution. Significant changes in the structure of the signals were observed between δ= 4 and 2 ppm upon coordination of the ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ to the Zn(II) ion. On the basis of the two-dimensional NMR spectra (COSY and HMBC) the assignment of all protons was possible (see supp. data). In this region, the singlet at 5.69 ppm (5.53 for free $\mathbf{L}^1$), and the triplet at 3.55 ppm (3.51 for free $\mathbf{L}^2$) were attributed to (C7)H in $[Zn(\mathbf{L}^1)]^{2+}$ and $[Zn(\mathbf{L}^2)]^{2+}$ respectively. The spectra displays separate signals for the axial and equatorial H(C4) protons for $[Zn(\mathbf{L}^1)]^{2+}$ and $[Zn(\mathbf{L}^2)]^{2+}$ allowing to AB pattern (^2J_H = 7,5 Hz).This fact can be explained by the electronic field generated by the zinc ion in its proximity, which polarizes the C–H bond differently in the axial or equatorial position relative to the metal ion. This polarization

induces the deshielding of the equatorial protons, which are pointing away from Zn^{2+}. The aromatic region of the ^{1}H NMR spectrum of $[Zn(\mathbf{L^1})]^{2+}$ presents two signals at δ= 8.00 (singlet) and 7.45–7.35 ppm (multiplet) that correspond to (C6)H and aromatic protons respectively (see Figure 5) and presents one signal at 8.17 ppm for $[Zn(\mathbf{L^2})]^{2+}$that correspond to the triazolic proton.

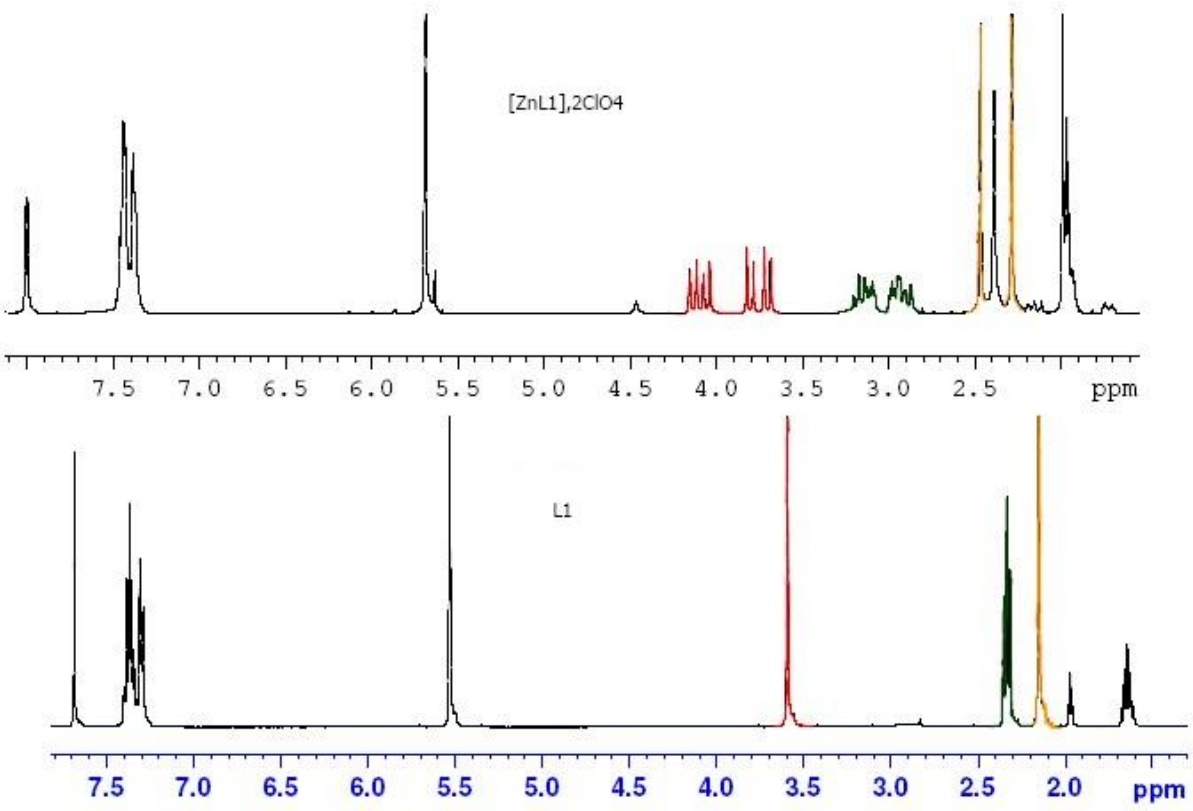


Figure 5: 300 MHz ^{1}H NMR spectra of $\mathbf{L^1}$ (spectrum a) and $[Zn(\mathbf{L^1})]^{2+}$(spectrum b), recorded in a CD_3CN solution at 298 K.

Conclusion

Novel acyclic hydrosoluble ligand with two 1,4-substituted-triazole moieties as coordinating side-arms (i.e. $\mathbf{L^2}$) was easily prepared in one step from a commercial N,N-dimethyl-propyl diamine via the Cu(I)-catalyzed Huisgen dipolar cycloaddition. This ligand bears the propanol moiety as hydrosolubilizing group to increase solubility in water. This compound readily form stable mononuclear 1:1-complex with M(II) in solution, with square-based pyramidal geometry. The behaviours of the reported metal transition complexes suggest that these complexes could be proposed as catalyst (e.g. for the oxidation of alcohols in carbonyl compounds or as artificial enzymes). First studies of the catalytic activity and cytotoxicity of these complexes towards uterine human sarcoma cells are currently underway and showed promising activities.

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