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Artigo

SYNTHESIS, STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF ZINC AND COPPER COMPLEXES BASED ON SULFONAMIDES CONTAINING 8-AMINOQUINOLINE LIGANDS

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Sulfonamides obtained by reaction of 8-aminoquinoline with 4-nitrobenzenesulfonylchloride and 2,4,6-triisopropylbenzenesulfonyl chloride were used to synthesize coordination compounds with Cu^{II} and Zn^{II} with a ML_2 composition. Determination of the crystal structures of the resulting zinc and copper complexes by X-ray diffraction show a distorted tetrahedral environment for the $[Cu(qnbsa)_2]$, $[Cu(qibsa)_2]$ and $[Zn(qibsa)_2]$ complexes in which the sulfonamide group acts as a bidentate ligand through the nitrogen atoms from the sulfonamidate and quinoline groups. The complex $[Zn(qnbsa)_2]$ crystallizes with a water molecule from the solvent and the Zn is five-coordinated and shows a bipyramidal-trigonal geometry. The electrochemical and electronic spectroscopy properties of the copper complexes are also discussed.

Keywords: copper; zinc; sulfonamide complexes.

INTRODUCTION

The coordination chemistry of sulfonamides has undergone noticeable development in recent years due to the interesting properties of these substances, such as SOD mimetic activity[1] and chemical nucleases. Complexes based on sulfonamides as ligands are artificial chemical nucleases that degrade DNA in the presence of sodium ascorbate. A recent study of the radical scavengers revealed that the ROS (reactive oxygen species) involved in the DNA damage were hydroxyl, singlet oxygen-like species, and superoxide anion.[2] The interaction of these complexes with DNA has gained much attention due to possible applications as new therapeutic agents.

Of particular interest are some metalloprotease inhibitors belonging to this class, which by inhibiting several matrix metalloproteases (MMPs) show interesting antitumor properties. Some of these compounds are currently being evaluated in clinical trials. The large number of sulfonamide MMP inhibitors ultimately reported also lead to the design of effective tumor necrosis factor-α converting enzyme (TACE) inhibitors, potentially useful in the treatment of inflammatory states of various types.[3]

Thus, copper complexes are known to be promising reagents for the cleavage of nucleic acids.[4] Moreover, organic copper complexes based on a quinoline ring system have also been investigated as potential and selective proteasome inhibitors in human cancer cells, as well as their biological activity toward the cell viability was verified, focusing in the capability of inducing the apoptotic process.[5]

On the other hand, zinc is an essential element for humans and plays an important role in biochemical and nutritional processes. Zinc complexes are of great interest in organic synthesis and bioinorganic chemistry. In the former, zinc complexes are used in stereospecific organic reactions.[6] In bioinorganic chemistry, it is well known that zinc plays an important role in many biological processes, and Zn^{II} coordinated by a strategic ligand can thus lead to a structural and/or functional model for zinc metalloenzymes.[7] In addition, many compounds with zinc and copper have been prepared and their applications in metal-specific fluorescence probes have been investigated.[8,9] Moreover, the 8-aminoquinoline scaffold is one of the most widely employed molecular platforms to construct many ionophoric system for the recognition of important metal ions such as Zn^{+2} and Cu^{+2}.[10] Among many of the functional transformations, the incorporation of the sulfonamide group is plausible for the construction of more elaborate functional chemosensors.[11] Thus, several quinoline-based compounds, such as TSQ [6-methoxy-8-(4-tolylsulfonamido) quinoline] and zinquin, have been employed to detect zinc in living systems.[12] The properties of this class of compounds were established by X-ray crystallo-graphy, potentiometry, fluorescence microscopy and UV-visible.[13] These results reveal interesting features and provide a structural basis to understand the mechanism of Zn(II)-specific fluorescence indicators, and establish a foundation for the design of additional intracellular probes of metal ion chemistry.

Recent antiprotozoal approaches have hampered to search for new lead compounds based on 8-aminoquinoline derivatives with reduced toxicity and superior therapeutic utility.[14] In this context, we have assayed *N*-quinolin-8-yl-arylsulfonamides and two of their copper and zinc complexes against both extra and intracellular forms of *Leishmania amazonensis, L. chagasi and Trypanosoma cruzi* and showed high antiprotozoal activity.[15]

In the light of this interest, we here describe the synthesis and characterization of two sulfonamides derived from 8-aminoquinoline with 4-nitrobenzenesulfonylchloride and 2,4,6-triisopropylbenzenesulfonyl chloride as well as their zinc and copper complexes. Detailed spectroscopic (UV-Vis and EPR) and electrochemical properties of the copper(II) complexes are also discussed in this article. The X-ray crystal structures of the complexes have been already reported in the literature.[16-19]

EXPERIMENTAL

Physical measurements

IR spectra were recorded on a Perkin Elmer 2000 FTIR spectrophotometer using KBr pellets. Electronic spectra were recorded

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on a Pelkin Elmer UV–Vis/NIR Diode Array spectro-photometer in the 280-800 nm range. Cyclic voltammetry was performed using an Epsilon EC 2000 Potentiostat (working electrode: glassy carbon, reference electrode: Ag/Ag^+, support electrode: platinum, support electrolyte: tetrabutylammonium hexafluorophosphate and internal standard: ferrocene). Electronic Paramagnetic Resonance experiments were performed on an EPR BRUKER ESP 300E spectrometer (standard concavity: 4102-SP, frequency X band 9.5 GHz) at 293K and 77K, using liquid N_2. The 300 MHz ^1H spectra were recorded on a Bruker AC 300 FT spectrometer. Chemical shifts are reported as % values (ppm) downfield from Me_4Si. Mass spectrometry was performed on a Bruker-Franzen Esquire LC mass spectrometer. Thin-layer chromatography (TLC) was carried out using aluminium sheets pre-coated with silica gel 60 F254 (0.2 mm; E. Merk).

Materials

8-Aminoquinoline and the sulfonyl chlorides were provided by Aldrich and Fluka, respectively, and all reagents were of analytical grade and used as received.

Synthesis of the ligands

Compound 4-nitro-*N*-(8-quinolyl)benzenesulfonamide **(qnbsa)** (Figure 1 – A) and 2,4,6-triisopropyl-*N*-(8-quinolyl) benzene-sulfonamide **(qibsa)** (Figure 1 – B) were prepared by direct synthesis of the 8-aminoquinoline with the corresponding sulfonyl chloride, using pyridine as the solvent according to a procedure given in the literature.[20,21]

Analytical Data: **(qnbsa)** Colorless crystalline solid. Yield (84%). m.p.:170 °C. ^1H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.26-7.54 (m, 4H); 7.93 (dd, *J*= 1.6 and 8 Hz, 1H); 8.08 (t, *J*= 6 Hz, 2H) 8.14 (t, *J*= 8 Hz, 2H); 8.78 (dd, *J*= 1.6 and 6 Hz, 1H); 11.45 (s, 1H). MS m/z: 329 M^+. **(qibsa)** Colorless crystalline solid. Yield (65%). m.p.:141 °C. ^1H NMR ($CDCl_3$, 300 MHz, ppm) δ 1.27 (s, 18H); 2.82 (m, 1H); 4.37 (m, 2H); 7.09 (s, 2H); 7.25-7.46 (m, 4H); 7.68 (dd, *J*= 2 and 6.7 Hz, 1H); 8.09 (dd, *J*= 1.6 and 6 Hz, 1H); 8.74 (dd, *J*= 1.6 and 6 Hz, 1H); 9.31 (s, 1H). MS m/z: 410.

Synthesis of the complexes

Aqua-bis[4-nitro-*N*-(quinolin-8-yl)benzenesulfonamidato-κ^2N,N´]zinc(II) **($[Zn(qnbsa)_2]$)** and bis[2,4,6-triisopropyl-*N*-(quinolin-8-yl)benzenesulfonamida to-κ^2*N*,*N*'] zinc(II) **($[Zn(qibsa)_2]$)** were prepared according to a procedure found in the literature.[22] 1.5 mmol of the sulfonamide **(qnbsa)** or **(qibsa)** were dissolved in 75 mL methanol and 2 mL 2M NH_4OH were added. While this solution was magnetically stirred, 0.75 mmol of $ZnCl_2$ dissolved in 50 ml methanol were added dropwise. When addition was completed a yellow precipitate was formed which was separated by filtration. Yield: 80%.

Bis[4-nitro-*N*-(quinolin-8-yl)benzenesulfonamidato-κ^2*N*,*N*'] copper(II) **($[Cu(qnbsa)_2]$)** and bis[2,4,6-triisopropyl-N-(quinolin-8-yl)benzenesulfonamidato-κ^2*N*,*N*'] copper (II) **($[Cu(qibsa)_2]$)** were prepared according to a procedure given in the literature.[23] Into 50 mL of a methanolic solution of copper (II) acetate (0.1996 g, 1 mmol), 100 mL of a methanolic solution containing (2 mmol) of the ligands **(qnbsa)** or **(qibsa)** was slowly added under stirring. The solution became dark and after one day the crystals appeared (yield: 90%).

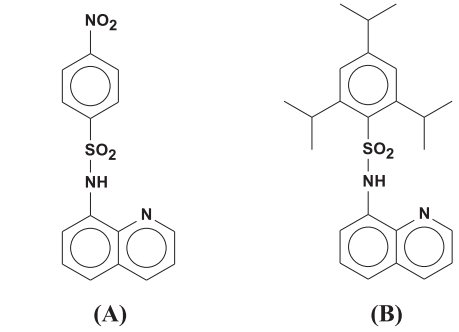


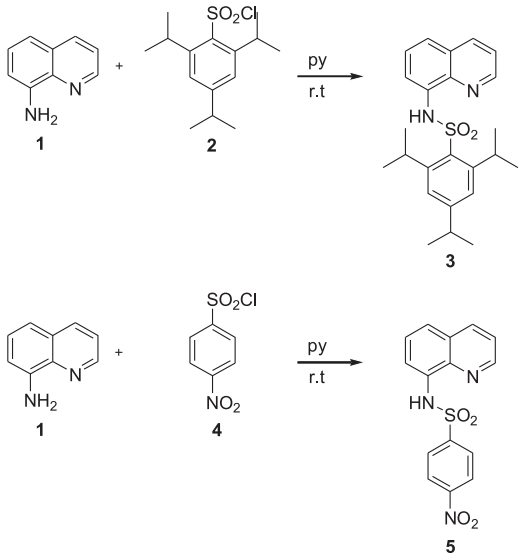
Figure 1. *The ligands 4-Nitro-*N*-(8-quinolyl)benzenesulfonamide* ***(A)*** *and 2,4,6-Triisopropyl-*N*-(8-quinolyl)benzenesulfonamide* ***(B)***

RESULTS AND DISCUSSION

Characterization of zinc and copper complexes

Mass spectroscopy and crystal structure

The structures of the two sulfonamides synthesized (**3** and **5**) are outlined in Scheme 1.



Scheme 1. *Structure of the qibsa (**3**) and qnbsa (**5**)*

The zinc complexes were prepared by direct reaction between the sulfonamide ligands and $ZnCl_2$. Although the copper complexes were prepared in a neutral medium, addition of a base to deprotonate the amine nitrogen atom was necessary to prepare the zinc complexes.

The formulae $[Zn(C_{15}H_{10}N_2O_4S)_2.H_2O]$ and $[Zn(C_{24}H_{29}N_2O_2S)_2]$ are in agreement with the mass spectral data. Complex $[Zn(qibsa)_2]$ shows a signal peak at m/z= 882 , which coincides with that of the molecular ion. Loss of one of the ligands is in agreement with a peak at m/z=617, also recorded. Complex $[Zn(qnbsa)_2]$ shows one peak at m/z= 720 which coincides with that of the molecular ion once the water molecule has been removed, probably weakly bound to the Zn(II). Loss of one of the ligands is in agreement with a peak at m/z=329, also recorded. Reaction of these sulfonamides with Cu(II) acetate deprotonates the N(sulfonamidate) atom, thus coordinating through both N atoms to yield complexes with a ML_2 stoichiometry, that is, $[Cu(qnbsa)_2]$ **(6)** and $[Cu(qibsa)_2]$ **(7)**. These formulae are also in agreement with the mass spectrum data. Complex $[Cu(qnbsa)_2]$ **(6)** shows a signal peak at m/z= 720, which coincides with that of the molecular ion. Loss of one of the ligands is in agreement with a peak at m/z=/347, also recorded. Complex

$[Cu(qibsa)_2]$ **(7)** shows two important peaks at m/z=882 and 449, corresponding to the molecular ion and to a $[Cu(qibsa)]^+$ fragment, respectively.

The molecular structure of the complexes $[Zn(qibsa)_2]$[16] and $[Zn(qnbsa)_2]$[17] are shown in Figure 1S. The structure of $[Zn(qibsa)_2]$ corresponds to a highly distorted tetrahedron, where the sulfonamide acts as a bidentate ligand. The $Zn\text{-}N_{(quinoline)}$ bond lengths [2.074 and 2.049 Å] are slightly larger than the Zn-N(sulfonamide) bonds [1.972 and 1.974 Å], which are in the usual range.

The complex $[Zn(qnbsa)_2]$ crystallizes with a water molecule from the solvent. The Zn is five-coordinated and shows a bipyramidal-trigonal geometry.

The crystalline structure of the complexes $[Cu(qnbsa)_2]$[18] and $[Cu(qibsa)_2]$[19] are shown in Figure 2S. Copper is four-coordinated with two nitrogen atoms from each of the two quinolinesulfonamidate ligands. Cu–O distances are larger than 2.9 Å, so there is no interaction between copper and oxygen atoms. The geometry around the copper can be best described as square planar for $[Cu(qnbsa)_2]$ and see saw for $[Cu(qibsa)_2]$. Sulfonamide acts as a bidentate ligand, forming five membered rings. The Cu-N distances are similar to those found in similar copper complexes,[23,24] although the $Cu\text{-}N_{(sulfonamide)}$ are slightly shorter than the $Cu\text{-}N_{(quinoline)}$ distances, 1.943 Å versus 1.996 Å for $[Cu(qnbsa)_2]$ and 1.926 Å and 2.024 Å for $[Cu(qibsa)_2]$, respectively.

FT-IR spectroscopy

The IR spectra were not studied in detail: only the characteristic vibrations were interpreted. The positions of the most significant bands are shown in Table 1. Note the two bands due to the vibrations of the SO_2 group.[25]

Table 1. Selected IR bands (cm^{-1})

Compound	SO_2	N-H	S-N	C-S	NO_2	$CH(CH_3)_2$
$[Zn(qnbsa)_2]$	1129	-	956	610	1524, 1320 and 853	-
$[Zn(qibsa)_2]$	1129	-	949	655	-	2960
$[Cu(qnbsa)_2]$	1144	-	956	614	1526, 1347 and 864	-
$[Cu(qibsa)_2]$	1131	-	947	656	-	2960

An important feature in the spectrum of the complexes is that the band at 3260 cm^{-1}, present in the spectrum of the ligand νN-H, does not appear, indicating deprotonating of the amino group.

UV-Vis spectroscopy

The electronic spectra of the zinc complexes (Table 2) in DMF solution show a band at 362 - 375 nm attributed to a $p\pi \rightarrow p\pi^*$ internal ligand charge transfer. The complex **$[Cu(qnbsa)_2]$** in DMF solution shows only a band at 360 nm corresponding the (LMCT) processes because of the high value of ε (10200 L $mol^{-1}cm^{-1}$). For the complex **$[Cu(qibsa)_2]$** in DMF solution five bands can be attributed: 316 nm $p\pi \rightarrow p\pi^*$ internal ligand charger transfer, 380 nm $p\pi \rightarrow d\pi^*$ charge transfer (LMCT) and 488, 568 and 750 nm d–d transition in agreement with the highly distorted coordination environment around the Copper(II) center.

Cyclic voltammetry

The electrochemical behavior of compounds was studied by cyclic voltammetry. Cyclic voltammograms were recorded in DMF in the potential range -2.0 to 2.0V versus Ag/Ag^+, using $[TBA][(PF)_6]$ as the supporting electrolyte. For the zinc complexes only the cathodic or anodic wave of the ligand was observed in Figure 3S. The non-reversibility of the redox processes is indicative of the instability of the totally reduced or oxidized species in solution.

Table 2. UV-Vis spectral properties of the complexes (solution of DMF, [c]≈ 5.10^{-5} mol/L)

Compounds	color	Uv-vis (nm)	ε ($L.mol^{-1}.cm^{-1}$)	Transitions
$[Zn(qnbsa)_2]$	Yellow	362	7500	$p\pi \rightarrow p\pi^*$
$[Zn(qibsa)_2]$	Light Yellow	375	4280	$p\pi \rightarrow p\pi^*$
$[Cu(qnbsa)_2]$	Dark green	360	10200	$p\pi \rightarrow d\pi^*$
$[Cu(qibsa)_2]$	Brown	316, 380, 488, 568, 750	4900, 5200, 700, 730, 240	$p\pi \rightarrow p\pi^*$, $p\pi \rightarrow p\pi^*$ d-d (Cu)

For the **$[Cu(qnbsa)_2]$** and **$[Cu(qibsa)_2]$** complexes, one *quasi*-reversible redox process occurs at $E_{½}$ = -0.202 V and $E_{½}$ = -0.530 V versus NHE (ΔE_p = 0.08 V), respectively, attributed to the $Cu^{II} \rightarrow Cu^{I}$ process. Repetitive CV scans of these systems showed the maintenance of the CV curve profile with no significant decrease in either cathodic or anodic waves (Figures 2 and 4S – Table 3). The anodic shift of approximately 0.3 V for **$[Cu(qnbsa)_2]$** is most probably due to the electron withdrawing effect of the nitro substituent on the sulfonamide ligand.

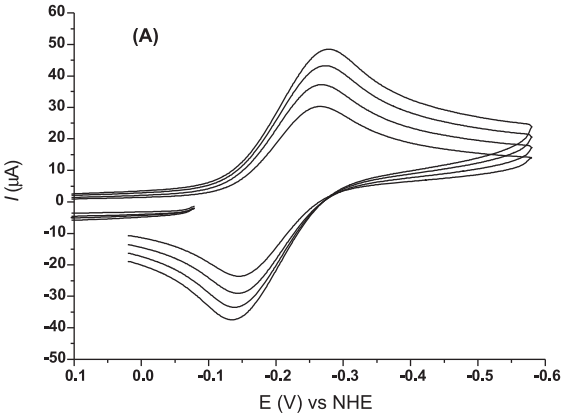


Figure 2. *Cyclic voltammogram of $[Cu(qnbsa)_2]$ and in DMF ((0.1 mol L^{-1}) $[Bu_4N][PF_6]$ supporting eletrolyte, glassy carbon working electrode, ferrocene internal standard, scan rate 25 - 500 mV s^{-1})*

Table 3. Electrochemical properties of Cu(II) complexes (v=100mV)

Complex[a]	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	i_{pa} (μA)	i_{pc} (μA)	i_{pc}/i_{pa}
$[Cu(qnbsa)_2]$	-0.172	-0.072	-0.122	-0.167	-0.083	0.42
$[Cu(qibsa)_2]$	-0.398	-0.318	-0.450	-0.400	-0.313	0.78

[a]Medium, DMF/0.1 M tetrabutylammonium hexafluorophosphate ($[TBA]PF_6$); concentration of the complexes 0.1 mM; Reference electrode Ag/Ag^+, $[TBA]PF_6$ 0.1 M in DMF. This electrode is at approximately 0.08 V vs the NHE at 25 °C.

Resonance paramagnetic electronic

The complexes **$[Zn(qnbsa)_2]$** and **$[Zn(qibsa)_2]$** did not show an EPR signal in (Zn^{2+} - d^{10}). The solution (DMF) of **$[Cu(qnbsa)_2]$** and **$[Cu(qibsa)_2]$** at 77 K (Figures 3 and 5S) provided an essentially axial EPR signal which was simulated using an S = ½ spin Hamiltonian, and the resulting fit provided g and A values in Table 4.

Both complexes show a similar single broad absorption band.[26] The absence of hyperfine lines in these complexes may be due to the

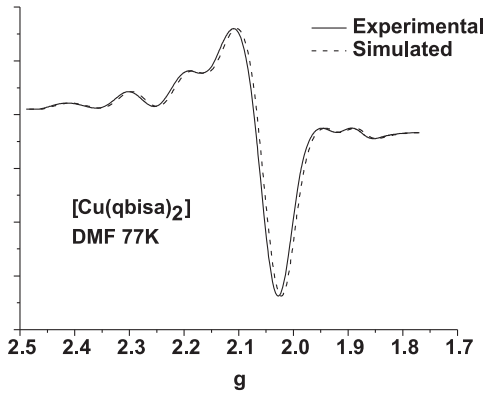


Figure 3. *X-band EPR spectra for copper complexe [Cu(qibsa)$_2$] in the frozen DMF solution. (—) Experimental spectrum and (…) simulated spectrum using the Winepr SimFonia® Program*

Table 4. EPR parameters of [Cu(qnbsa)$_2$] and [Cu(qibsa)$_2$] complexes

Complex[a]	$g_{//}$	$g_{\perp}$ [b]	g_0	A//	$A_{\perp}$ [c]	A_0	G[d]	$g_{//}/g_{\perp}$
[Cu(qnbsa)$_2$]	2.2807	2.075	2.143	121	52	75	3.7	1.01
[Cu(qibsa)$_2$]	2.2465	2.070	2.1288	145	33	70	3.5	1.08

[a] All coupling constants units 10^{-4} cm^{-1}. [b] $g_{\perp} = ½(3g_0 - g_{//})$. [c]$A_{\perp} = ½(3A_0 - A_{//})$. [d] $G = (g_{//} - 2)/(g_{\perp} - 2)$. The parameters $g_{//}$, $g_{\wedge}$ and $A_{//}$ was obtained from WinEPR Simfonia®.

strong dipolar and exchange interactions between the copper (II) ions in the unit cell.[27] The calculated $g_{//}$ and $g_{\perp}$ values appeared in the 2.28-2.24 and 2.070-2.075 regions, respectively, which supports the fact that $^2B_{1g}$ is the ground state, having an unpaired electron in the $d_{x^2-y^2}$ orbitals.[28] Both complexes show $g_{//} < 2.3$. It should be noted that for an ionic environment, $g_{//} > 2.3$, whereas for a covalent environment $g_{//} < 2.3$, indicating that the present complexes exhibit appreciable covalent natures. The G values are related by the expression $G = (g_{//} - 2) / (g_{\perp} - 2)$, and lie in the range 3.50-3.70, indicating a significant exchange interaction between the Cu^{+2} ions in the unit cell of these complexes, as the G values are less than 4.[29]

CONCLUSION

In summary, we have synthesized and characterized four zinc and copper complexes based on sulfonamides containing 8-aminoquinoline. These complexes were structurally characterized via X-ray crystallography, confirming that M^{II} occupies highly distorted tetrahedral environments in the [Cu(qnbsa)$_2$], [Cu(qibsa)$_2$] and [Zn(qibsa)$_2$] complexes with the sulfonamide group acting as a bidentate ligand through the nitrogen atoms from the sulfonamidate and quinoline groups. In addition, the complex [Zn(qnbsa)$_2$] crystallizes with a water molecule from the solvent and the Zn is five-coordinated which shows a trigonal bipyramid geometry. Moreover, deprotonation of the sulfonamide groups to coordinate the metal cation is also responsible for the lack of bands close to 3200 cm^{-1}. The EPR spectra of [Cu(qnbsa)$_2$] and [Cu(qibsa)$_2$] are characteristic of a copper(II) in a distorted tetrahedral arrangement and are in agreement with their crystal structures. Further studies involving these complexes as chemical nucleases are underway and will be the subject of future reports.

SUPPLEMENTAL MATERIALS

Molecular Structure of copper and zinc complexes as well as cyclic voltammogram and EPR spectra for copper complexes is free available from http:/quimicanova.sbq.org.br as pdf file.

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SYNTHESIS, STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF ZINC AND COPPER COMPLEXES BASED ON SULFONAMIDES CONTAINING 8-AMINOQUINOLINE LIGANDS

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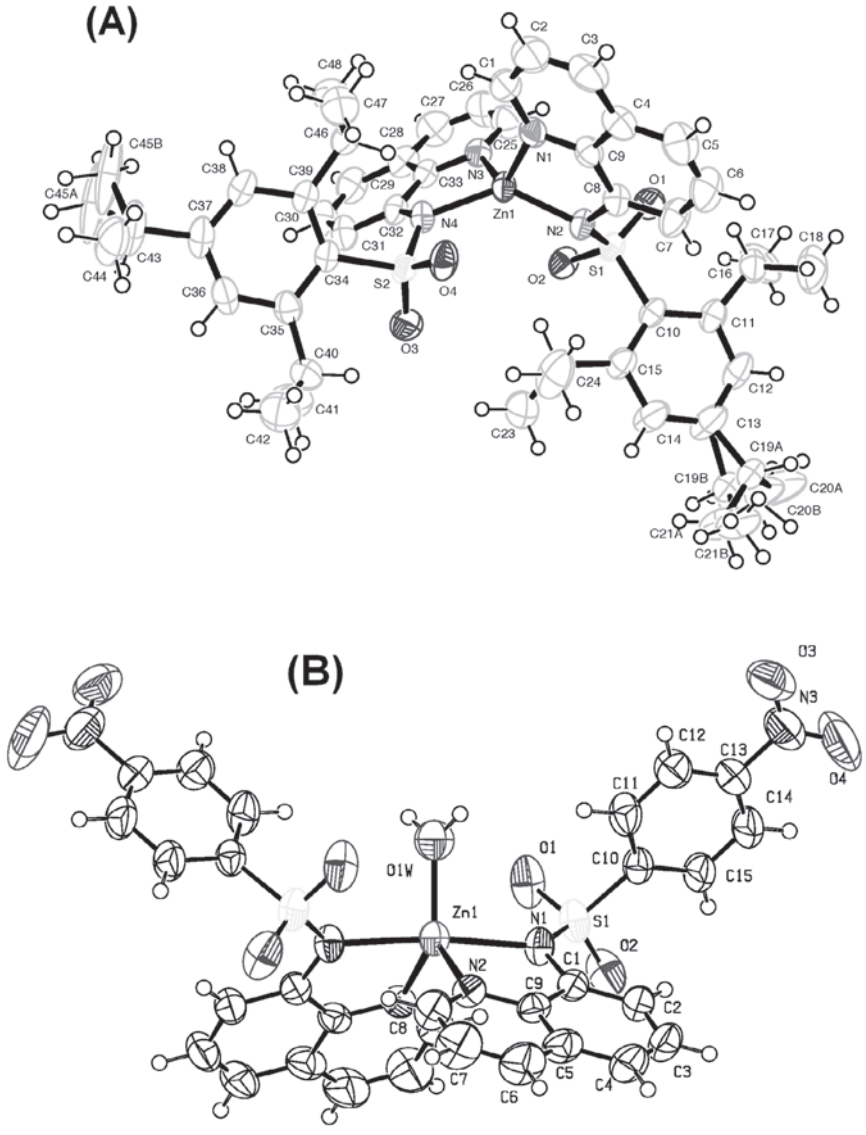

Figure 1S**. Molecular Structure of the [Zn(qibsa)$_2$] **(A)** and [Zn(qnbsa)$_2$] **(B)

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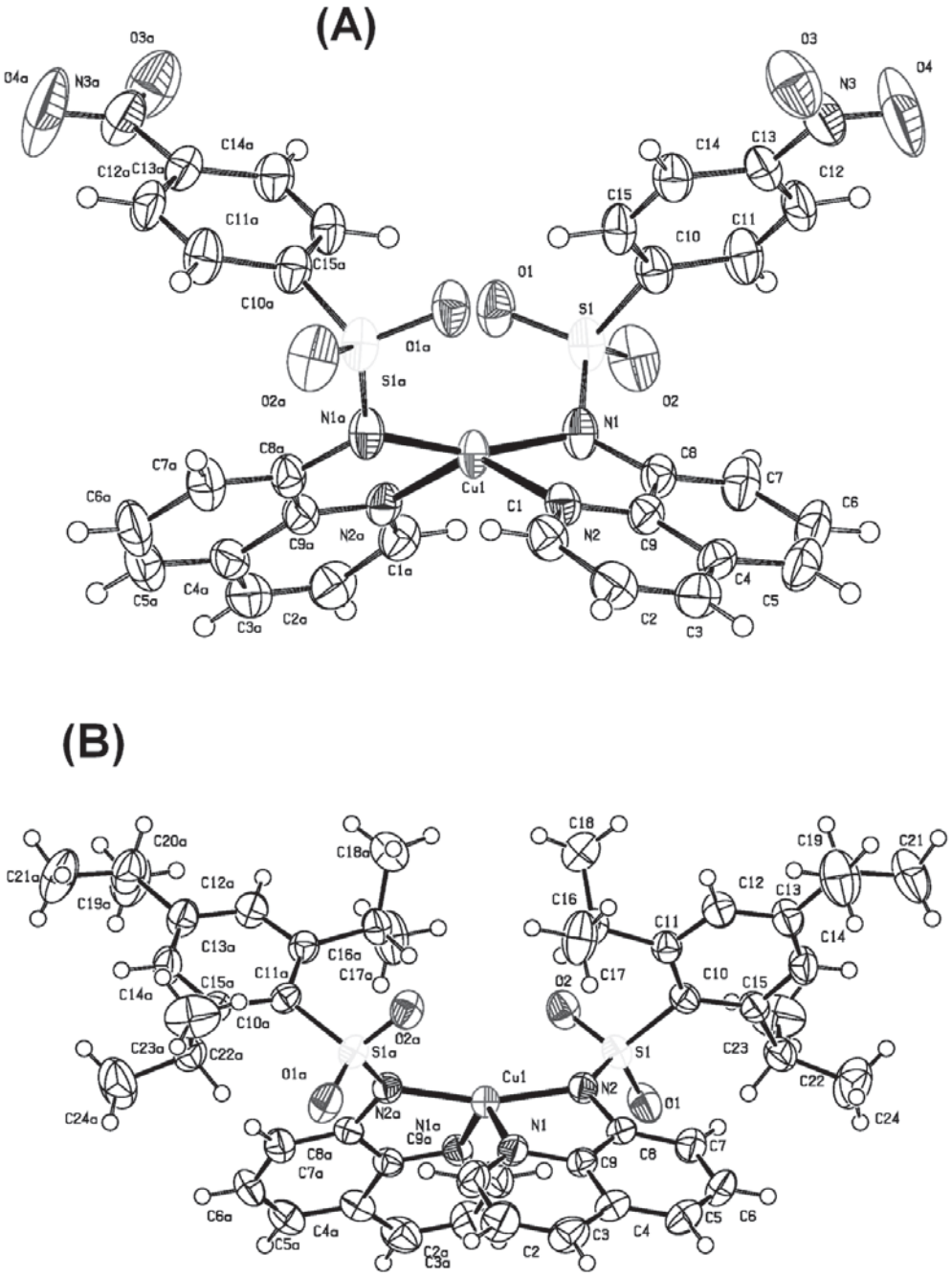

Figure 2S**. Molecular Structure of the [Cu(qnbsa)$_2$] **(A)** and [Cu(qibsa)$_2$] **(B)

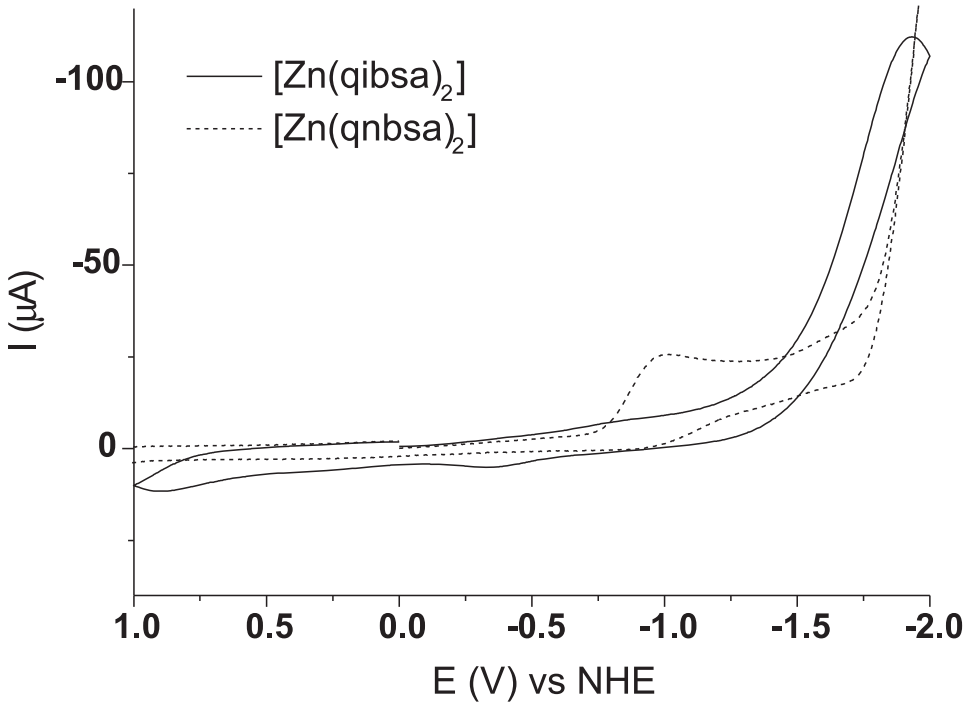

***Figure 3S**. Cyclic voltammogram of zinc complexes in DMF ((0.1 mol L^{-1}) $[Bu_4N][PF_6]$ supporting electrolyte, glassy carbon working electrode, ferrocene internal standard, scan rate 100 mV s^{-1})*

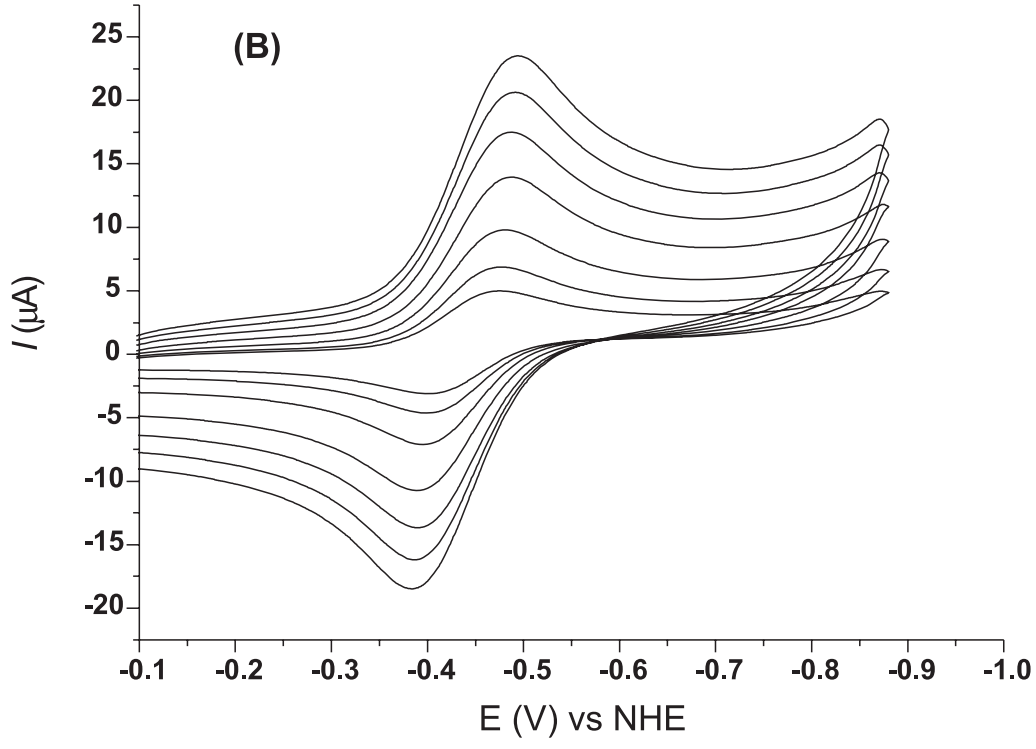

***Figure 4S**. Cyclic voltammogram of $[Cu(qibsa)_2]$ complexes in DMF ((0.1 mol L^{-1}) $[Bu_4N][PF_6]$ supporting eletrolyte, glassy carbon working electrode, ferrocene internal standard, scan rate 25 - 500 mV s^{-1})*

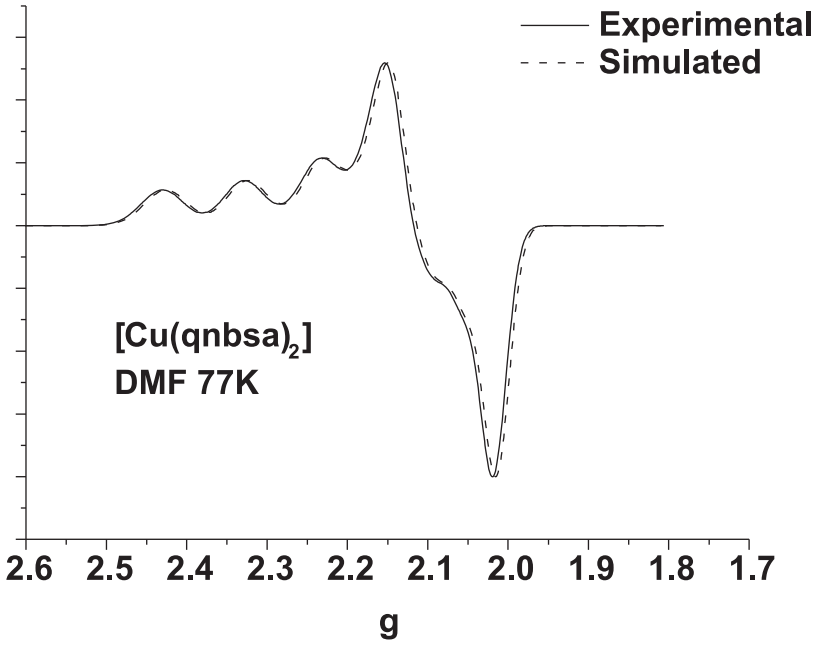

Figure 5S. *X-band EPR spectra for copper complexes in the frozen DMF solution. (—) Experimental spectrum and (…) simulated spectrum using the Winepr SimFonia® Program*