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## ARTICLE

## Tris-pyridylmethylamine (TPMA) complexes functionalized with persistent nitronyl nitroxide organic radicals

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The chance to have persistent organic radicals in combination with metals has large interest since it offers the possibility to have new functional molecules with multiple open-shell elements. In this study we report the synthesis of two tripodal tris(2-pyridyl)methylamine ligands (TPMA) functionalized with nitronyl nitroxide persistent radical. The newly formed ligands have been used to coordinate zinc(II), copper(II), iron(II) and cobalt(II). The resulting complexes have been investigated by means of Electron Paramagnetic Resonance (EPR), ESI-MS, FT-IR and X-Ray diffraction. An electron reduction of the N-O radical moiety has been observed, depending on the metal used for the formation of the complex and from the reaction conditions. We have observed small ~~some~~ differences in the EPR spectra depending on the *meta* or *para* position of the radical moiety in the complex structure and some antiferromagnetic interactions between the paramagnetic M(II) ions and the radical species.

## Introduction

The design of new molecular materials composed by organic nitroxide radicals,<sup>1</sup> in particular coupled with open-shell metals,<sup>2</sup> have attracted great attention because of their possible applications in quantum computing, data storage and molecular spintronics.<sup>3</sup>

Many studies have focused on nitronyl nitroxide (NNO) radicals since they are stable under ambient conditions and they are easy to synthesize and functionalize.<sup>4</sup> In these studies, they often act as bridging ligands for paramagnetic metal ions giving as result the strongest possible magnetic exchange coupling.<sup>1</sup> This strategy has been used for the synthesis of many magnetic systems such as single-molecule magnets,<sup>5</sup> single-chain magnets,<sup>6</sup> and chiral magnets.<sup>7</sup>

While many ligands have been used in combination with NNO radicals, to the best of our knowledge, studies on tris(2-pyridylmethyl)amine tripodal ligands (TPMA) have not been reported.<sup>8</sup>

In this context, here we report the synthesis and characterization of a novel family of tris(2-pyridylmethyl)amine tripodal ligands (TPMA) metallic complexes functionalized with NNO radicals. TPMA are a class of ligands that are able to bind a large variety of metal complexes.<sup>9</sup> In our group, we have also

extensively used TPMA in the past years for their application in catalysis,<sup>10</sup> as probes for enantiomeric excess determination<sup>11</sup> and in the construction of supramolecular cages.<sup>12</sup> The present study is designed to gather information on: *i*) the synthesis two ligands embedding a persistent NNO radical unit in which the metal is not interacting “through resonance” with the organic radical, *ii*) the effect of the presence of the organic radical on the complexation capabilities of the modified TPMA, *iii*) some preliminary studies on the interaction among the metal centre and the NNO as function of their distance imposed by the two different ligands. For this purpose, different transition metal TPMA complexes of zinc(II), copper(II), cobalt(II) and iron(II) have been investigated and their magnetic properties have been studied mainly by Electron Paramagnetic Resonance (EPR). The structure of some of these complexes were also elucidated by X-ray analysis. It should be emphasized that the system has been specifically designed to avoid direct the interaction (*viz.* resonance) of the unpaired electron of the NNO unit with the metal centre, focusing only on the effect of through the space interactions.

## Results and discussion

## Synthesis and characterization of the ligands

Ligands **1a,b** (Scheme 1), consisting in TPMA core bearing a 3 or 4-formyl-phenyl substituent on one of the three arms was obtained in a two-steps synthesis. The first step was a reductive amination of the commercially available 6-bromo-2-pyridinecarboxaldehyde and di(2-picolyl)amine, followed by a Suzuki coupling with 3 or 4-formylphenyl boronic acid respectively.<sup>11</sup> The NNO derivatives **2a,b** were then synthesized, according to Ullman's procedure, with minor

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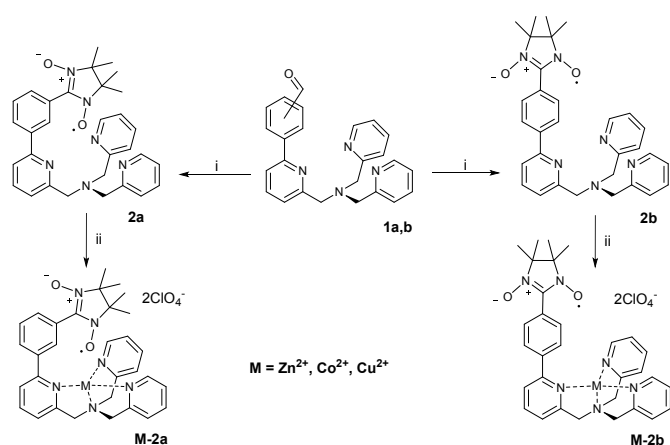
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modifications as shown in Scheme 1. In this case, the synthesis started from the commercial 2,3-dimethyl-2,3-dinitrobutane which was reduced with zinc in an ammonium chloride buffered solution to yield the key intermediate bis(hydroxylamine). A condensation between the latter and ligands **1a,b** formed the corresponding dihydroxy-imidazoline intermediates, generally less stable than the corresponding nitroxide derivatives. The dihydroxy-imidazoline intermediate of ligand **1b**, with the substituent in position 4 to the pyridine ring, precipitated in the reaction media as a white solid. Once filtered off, it was subsequently oxidized with  $\text{NaIO}_4$  to give the **NNO** derivatives **2b** as a blue solid, in good yields. On the contrary, it was not possible to isolate the dihydroxy-imidazoline intermediate of ligand **1a** which was directly oxidized to the **NNO** derivative **2a**. The mixture was then purified by precipitation in acetonitrile/diethyl ether, giving the desired compound as a blue solid in 50% yield. The low yields observed for these reactions were mainly related to the formation of by-products, derived by the electron reduction of the N-O moieties. As already known from the literature, this secondary reaction often occurs during the synthesis of **NNO** systems. The radical ligands **2a,b** were characterized by ESI-MS, FT-IR and EPR. FT-IR measurement showed for all the compounds the disappearance of the typical aldehydic carbonyl stretching in the region of  $1700\text{ cm}^{-1}$ , the appearance of the C=N and C-N bond stretching peaks in the region around  $\sim 1600$  and  $\sim 1400\text{ cm}^{-1}$  respectively, and N-O stretching at  $1575$  and  $1372\text{ cm}^{-1}$ . The EPR spectra of free ligands **2a,b** showed at 300 K in dichloromethane/toluene 1:1 the typical five lines of mono **NNO** radicals in isotropic conditions with relative intensities 1:2:3:2:1 because of the coupling of the unpaired electron with both the  $^{14}\text{N}$  atoms of the molecule, that resulted equivalent. Their corresponding  $g$  values were around 2.0065 and coupling constant with the nitrogens  $a_N$  around 7.5 G (see Figure S1 and S2). Traces of imino nitroxide impurities, formed after the oxidation of the dihydroxy-imidazoline intermediates, were present in both **NNO** derivatives **2a,b**. However, these impurities (lower than 3 %) detectable by EPR were not appreciable by ESI-MS.



**Scheme 1.** Synthesis of ligands **2a** and **2b** and corresponding Zinc, Copper and Cobalt(II) **M-2a,b** complexes. Reaction conditions: i) bis(hydroxylamine),  $\text{NaIO}_4$ , MeOH; ii)  $\text{M}(\text{ClO}_4)_2$ ,  $\text{CH}_3\text{CN}$ .

As expected, the EPR spectra obtained under frozen conditions (120 K) showed the typical anisotropic signal of a **NNO** radical (Figure S3 and S4).

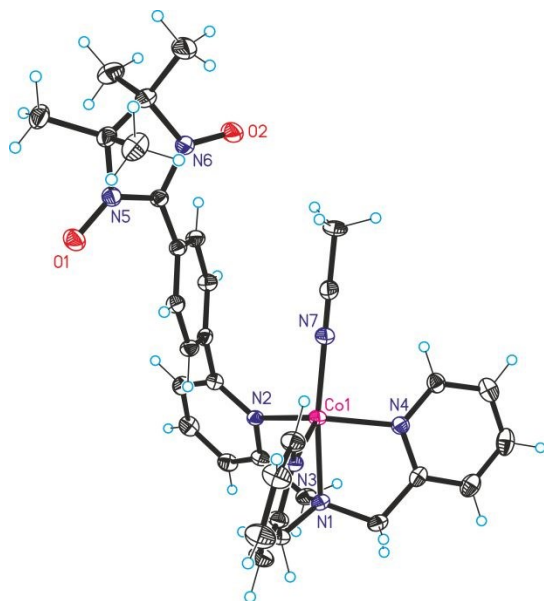
#### Synthesis and characterization of the Zn(II) complexes

The complexes **Zn-2a** and **Zn-2b** were obtained by mixing in acetonitrile, at room temperature, ligands **2a,b** with the commercial zinc(II) perchlorate salt (Scheme 1). Each reaction was let stirring 1 hour at room temperature and purified by precipitation followed by crystallization with diethyl ether. ESI-MS experiments, performed in acetonitrile, showed the characteristic isotopic cluster ions for both compounds. The EPR spectra of both **Zn-2a,b** complexes at 300 K were similar than the free ligands, but without appreciable imino nitroxide impurities (Figure S5 and S6). In frozen solution they also were similar, showing small differences in the  $A_x$  and  $g_x$  between them, obtained from their corresponding simulation (Figure S7 and S8).

(Figure 1 has been eliminated)

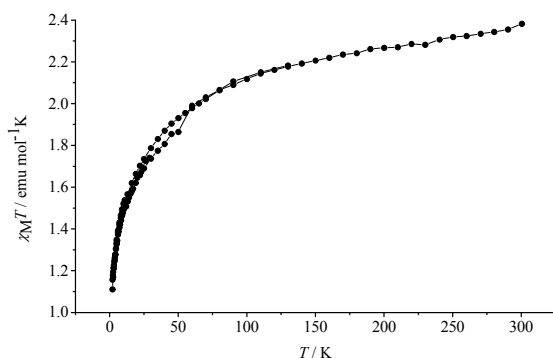
#### Synthesis and characterization of the Co(II) complexes

Complexes **Co-2a** and **Co-2b** were obtained by mixing in acetonitrile, at room temperature, ligands **2a,b** with the commercial cobalt(II) perchlorate salt and purified by crystallization with diethyl ether. ESI-MS showed the characteristic isotopic cluster ions confirming the formation of the desired compounds. Crystals suitable for X-Ray diffraction were obtained for **Co-2b** (Figure 1, Table S1). Both Co(II) complexes **Co-2a,b** displayed similar EPR spectra at 300 K than the free ligands **2a,b** (Figure S9 and S10). In frozen solution, we observed the anisotropic spectral pattern of the **NNO** radical but no clear signal assignable to a cobalt(II) ion was observed in any of them, only an almost unnoticeable signal in each case, which was even less intense in **Co-2b** compound (see Figure S11 and S12). This fact could be attributed to an antiferromagnetic coupling between the cobalt(II) and the radical ligand,<sup>13</sup> The temperature dependence of the molar magnetic susceptibility  $\chi_M$  was measured in the range of 2-300 K for complex **Co-2a** (Figure 2) by means of a SQUID magnetometry. A  $\chi_M T$  value of  $2.34\text{ emu K mol}^{-1}$  was obtained at 300 K, which is close to the theoretical one expected for two isolated  $S = 3/2$  ( $\text{Co}^{2+}$ ) and  $S = 1/2$  (**NNO**) spins in terms of the spin-only equation ( $\chi T = 0.12505 \cdot g \cdot 2[S(S+1)] = 0.12505 \cdot 2.2[3/2(3/2+1) + 1/2(1/2+1)] = 2.25$ ). With decreasing the temperature  $\chi_M T$  decreased continuously, indicating antiferromagnetic interactions between the spin carriers.



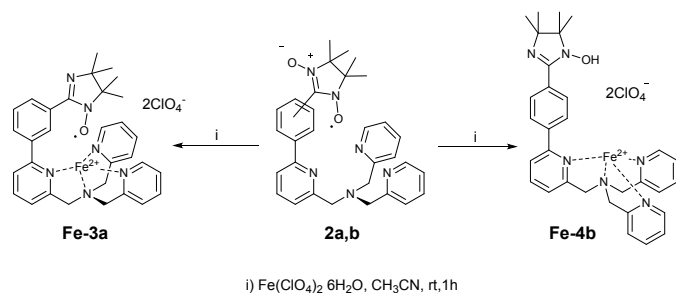
**Figure 1.** Cationic molecular structure of **Co-2b** complex, showing thermal ellipsoids at 25% probability. Selected distances and angles in Å and °: Co-N1 2.163(3), Co-N7 2.042(3), Co-N2 2.095(3), Co-N3 2.039(3), Co-N4 2.065(3), N5-O1 1.285(4), N6-O2 1.283(4) and N1-Co-N7 173.16(12).

**Figure 2.** Temperature dependence of the molar magnetic susceptibility with temperature ( $\chi_M T$ ) of complex **Co-2a**.



### Synthesis and characterization of the Fe(II) complexes

The synthesis of iron(II) complexes **Fe-2a,b** was also investigated following the best conditions described for the parent compounds. However, a mixture of two radical species was obtained for the complex synthesized starting from ligand **2a** and iron(II) perchlorate. This type of reactivity has been already observed when **NNO** is in presence of iron(II)<sup>14</sup>



**Scheme 2.** Synthesis of compounds **Fe-3a** and **Fe-4b**.

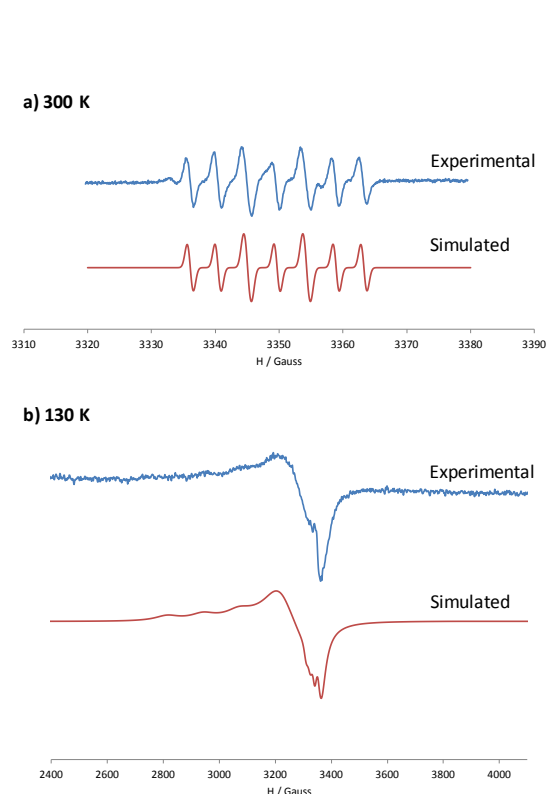
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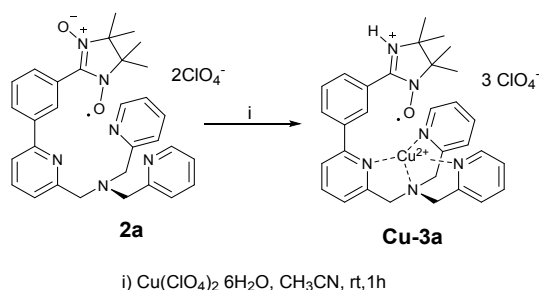
EPR spectral mixture was obtained, with the principal radical species being the imino nitroxide radical derivatives **Fe-3a**, and the second one containing 5 lines with  $a_{\text{N}(2\text{N})} = 4.9$  G from a radical species with two equivalent N, in a ratio 2.2:1, respectively (Figure S13-S14). ESI-MS  $m/z$  isotopic cluster ions also indicated that the principal product formed was **Fe-3a**. In frozen solution, we did not observe any ion metal signal (Figure S15) as it has been shown that Fe(II) complexes coordinated with *tris*-pyridylmethylamine ligands forms the low-spin complex in acetonitrile, thus, a diamagnetic species.<sup>15</sup> For the ligand **2b**, with the **NNO** in *para* position, no radical signal was detected by EPR and ESI-MS analysis, suggesting the formation of the non-radical derivative **Fe-4b** (Scheme 2). Change of reaction times or stoichiometry did not furnish better results indicating a lower compatibility of the iron(II) with the **NNO** radical.

### Synthesis and characterization of the Cu(II) complexes

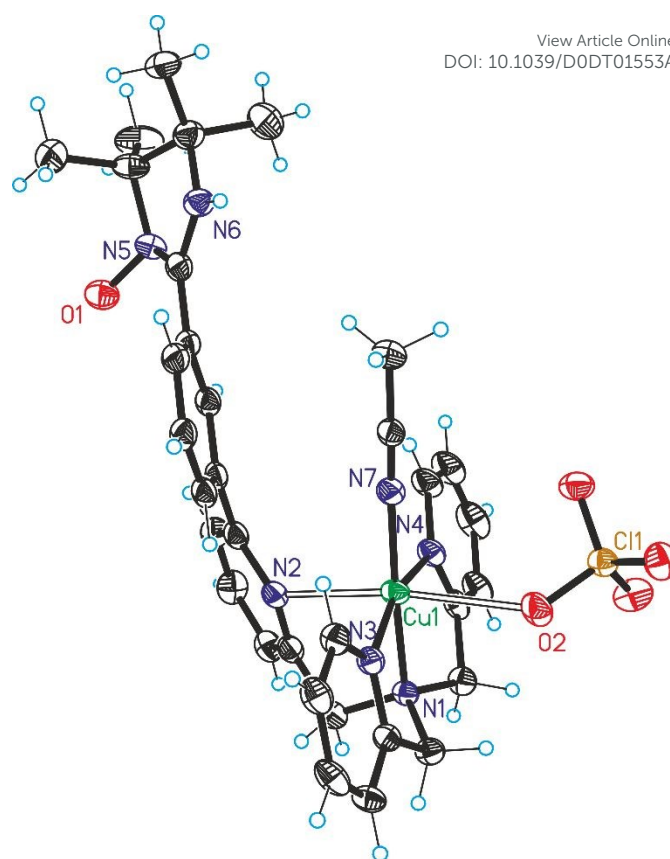
The procedure previously described for synthesizing zinc(II) and cobalt(II) TPMA complexes was followed to obtain the corresponding copper(II) system **Cu-2a,b** (Scheme 1). Ligands **2a,b** were mixed with a small excess of the perchlorate metallic salt (less than 1.2 equivalents) to ensure the reaction completeness, and the reaction was let stirring 1 hour at room temperature. However, following these experimental conditions, the EPR spectrum at 300 K of the copper(II) derivative using ligand **2a** showed seven lines with  $a_{\text{N}1} = 4.35$  G and  $a_{\text{N}2} = 9.20$  G at  $g$ -factor = 2.0066 (Figure 3a), indicating the loss of an oxygen atom from the **NNO** structure typical of an imino nitroxide radical species (obtaining of **Cu-3a**, Scheme 3), while using ligand **2b** we obtained a cleaner EPR spectrum at 300 K (~90% **NNO**, and 10% imino nitroxide), indicating the majority formation of **Cu-2b**. X-Ray diffraction analysis of the former **Cu-3a** (Figure 4, Table S2) confirmed the loss of an oxygen atom from the structure and showed that the radical species present was an iminium nitroxide (**Cu-3a**, Scheme 3). The structure showed a change in the coordination geometry from bipyramidal trigonal to octahedral. The EPR spectrum of such a complex in frozen solution (130 K, Figure 3b) also confirmed this geometry. Actually, the spectrum showed hyperfine splitting in the  $g_z$  region due to coupling of the unpaired electron to the  $^{63,65}\text{Cu}$  ( $I = 3/2$ ) nuclei; three of the four metal hyperfine lines were observed and the fourth was partially hidden in the  $g_{x,y}$  region.



**Figure 3.** Experimental and simulated EPR spectra of **Cu-3a** at a) 300 K ( $a_{N1} = 4.35$  G,  $a_{N2} = 9.20$  G,  $g = 2.0066$  and b) 130 K ( $A_{(x,x)} = 15$  G,  $A_{(y,y)} = 5$  G,  $A_{(z,z)} = 128$  G;  $g_x = 2.020$ ,  $g_y = 2.070$ ,  $g_z = 2.24$ ).



**Scheme 3.** Formation of compound **Cu-3a**.



**Figure 4.** Cationic molecular structure of **Cu-3a** complex, showing thermal ellipsoids at 25% probability. Selected distances and angles in Å and °: Cu-O2 2.559(4), Cu-N2 2.460(4), Cu-N1 2.021(4), Cu-N7 1.973(5), Cu-N3 1.995(4), Cu-N4 1.993(4), N5-O1 1.400(7) and O2-Cu-N2 166.15(15).

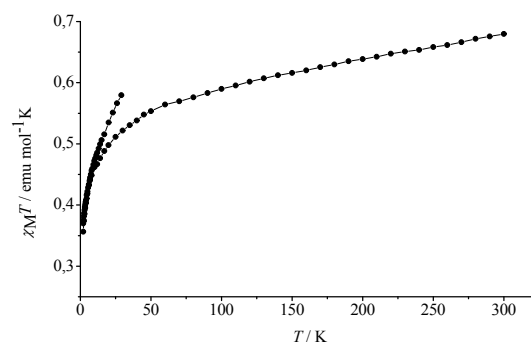
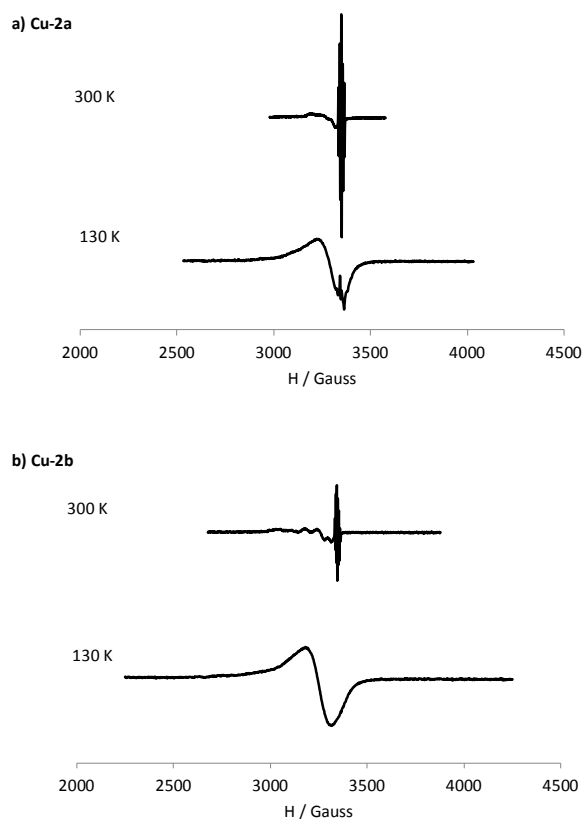
It exhibited a typical Cu(II) complex possessing a  $d_{x^2-y^2}$  ground state ( $S = \frac{1}{2}$ ) with  $g_z > g_x \approx g_y > g_e = 2.0023$  ( $g_z = 2.24$ ,  $g_y = 2.070$ ,  $g_x = 2.020$ ) characteristic of a Cu(II) complex with an elongated octahedral geometry.<sup>16</sup>

A decrease of the copper(II) perchlorate amount, together with a shorter reaction time, allowed for the synthesis of the desired copper(II) complex **Cu-2a** (Scheme 1). EPR spectrum analysis confirmed the purity of the compound showing the typical **NNO** five lines. Both, pure **Cu-2a** and **Cu-2b** complexes showed at 300 K not only the **NNO** radical signal but also the signal corresponding to a copper(II) ion (Figure 5). In frozen solution, we observed in both complexes the signal of copper(II) ion (Figure 5); in **Cu-2a** the  $g$  parameters obtained from the simulation (see Figure S16) were similar ( $g_z = 2.23$ ,  $g_y = 2.075$ ,  $g_x = 2.032$ ) to the ones from **Cu-3a** also fulfilling  $g_z > g_x \approx g_y > g_e$ , while in **Cu-2b** they were a little bit different, showing in this case completely axially symmetric  $g$ -tensor parameters ( $g_z = 2.23$ ,  $g_y = 2.075$ ,  $g_x = 2.075$ ) fulfilling  $g_z > g_x = g_y > g_e$  (see Figure S17). The temperature dependence of the molar magnetic susceptibility  $\chi_M$  was measured in the range of 2–300 K for complex **Cu-2a** (Figure 6) by means of a SQUID magnetometry. At room temperature, the value of the  $\chi_M T$  was  $0.70 \text{ emu K mol}^{-1}$  which corresponds to that calculated for a copper(II) and one **NNO** radical, i.e. two non-correlated  $S = \frac{1}{2}$  spins ( $0.750 \text{ emu K mol}^{-1}$ ). With decreasing the temperature  $\chi_M T$  decreased



continuously reaching around  $0.350 \text{ emu K mol}^{-1}$  at 2 K, close to the value of  $0.375 \text{ emu K mol}^{-1}$  expected for an isolated unpaired electron. This behavior is indicative of antiferromagnetic interactions between the spin carriers.

**Figure 5.** EPR spectra in solution at 300 K and frozen solution at 130 K of a) **Cu-2a** and b) **Cu-2b**.



**Figure 6.** Temperature dependence of the molar magnetic susceptibility with temperature ( $\chi_M T$ ) of complex **Cu-2a**.

## Conclusions

In this paper we have reported the successful synthesis of a new class of tetradentate ligands in which a persistent organic radical is embedded. The ligands have been used to coordinate four different metals and initial studies of their EPR spectra have been recorded. Interesting results have been obtained regarding the radical stability upon complexation. In addition, we have observed some influence of the *meta/para* position of the radical moiety on their corresponding EPR spectra, as well as some antiferromagnetic interactions between Co(II) and Cu(II) paramagnetic metal ions and the organic radical species, which seem more intense in the case of the *para* substituted complexes. Beside possible interest in the formation of paramagnetic materials, these novel complexes can also find further application in catalysis, where **TPMA** have already shown outstanding properties.

## Conflicts of interest

There are no conflicts to declare

## Acknowledgements

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## Notes and references

‡ CCDC-1997742 **Co-2b** and CCDC-1997743 **Cu-3a** contain crystallographic data and can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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