

# Synthesis and EPR Studies of Zinc and Copper Tris(2-pyridylmethyl)amines (TPMA) Metal Complexes Containing TEMPO Functionalities

Elena Badetti<sup>+</sup>,<sup>\*,[a, b]</sup> Vega Lloveras<sup>+</sup>,<sup>[c]</sup> Melvin Raulin,<sup>[a]</sup> Francesca A. Scaramuzzo,<sup>[a, d]</sup> Jaume Veciana,<sup>[c]</sup> José Vidal-Gancedo,<sup>\*,[c]</sup> Giulia Licini,<sup>[a]</sup> and Cristiano Zonta<sup>\*,[a]</sup>

A new family of stable radical-containing polytopic ligands based on tris(2-pyridylmethyl)amines TPMA architecture and their corresponding metal complexes have been synthesized. These molecular systems offered the possibility to investigate how various spin carriers, such as the metal ion and the organic

radical, influence their EPR properties mainly through the empirical ratio of peak heights  $d_x/d_y$ . Moreover, it has been possible to analyze how different conformations of TEMPO radical units in the molecular skeleton affect the metallic system.

## Introduction

In coordination chemistry, tris(2-pyridylmethyl)amines (TPMA) are a relatively new class of chelating ligands.<sup>[1]</sup> These tetradentate molecules are able to coordinate to a large variety of transition metals. Depending on the nature of the associated metal, these complexes have displayed various applications such as: catalysis (oxygen reduction, water oxidation, atom transfer radical polymerization, hydrogen production, ...),<sup>[2]</sup> molecular recognition,<sup>[3]</sup> chiral sensing,<sup>[4]</sup> imaging<sup>[5]</sup> and oxygen binding.<sup>[6]</sup> These features arise from the high stability of these ligands in presence of competing binders especially in catalysis. For this reason, several synthetic strategies have been developed to facilitate the preparation of these ligands, and robust post-functionalization methods of the formed ligands are reported.<sup>[7]</sup>

In recent years, we took advantage of the scaffold to organize spatially nitronyl nitroxide and TEMPO radicals and control radical-radical interactions.<sup>[8]</sup> In particular, we have evaluated how the chemistry of organic radical systems can be coupled with coordination chemistry to obtain novel properties.<sup>[9,10]</sup> The structural arrangement provided by the complex organization has been used to generate a novel class of redox mediators.

With this knowledge in hand, we started to investigate how and if organic radicals can interact with metals having unpaired electrons. For this reason, in this paper we report a series of TPMA metal complexes decorated with TEMPO radicals in different molecular arrangements. In particular, a comparison among Zn(II) and Cu(II) systems will be used as benchmark for the study of this interaction.

## Results and Discussion

The correlation study among different spin carriers has been planned synthesizing TEMPO metal systems by increasing the level of molecular complexity. In particular, the study was carried out using Zn(II) and Cu(II) complexes of TPMA in which one or three TEMPO organic radicals are covalently incorporated to the molecular skeleton (in *meta* or *para* conformation) or directly coordinated to the metal.

### Mono TEMPO-Functionalized TPMA Systems

#### Synthesis and Coordination Chemistry

The functionalization of tris(2-pyridylmethyl)amine TPMA ligands bearing an aldehyde moiety in *meta* or *para* position in respect to the pyridine ring started from compounds **1a** and **1b** (Scheme 1), which synthesis was already reported by our group.<sup>[4a,d]</sup> TEMPO functionalized ligands **2a,b** were prepared through an imine condensation reaction between the aldehyde

[a] E. Badetti,<sup>+</sup> M. Raulin, F. A. Scaramuzzo, G. Licini, C. Zonta  
Department of Chemical Sciences, University of Padova, Via Marzolo 1,  
35131 Padova, Italy  
E-mail: cristiano.zonta@unipd.it

[b] E. Badetti<sup>+</sup>  
Department of Environmental Sciences, Informatics and Statistics, University  
Ca' Foscari of Venice, Via Torino 155, 30172 Venice Mestre, Italy  
E-mail: elena.badetti@unive.it

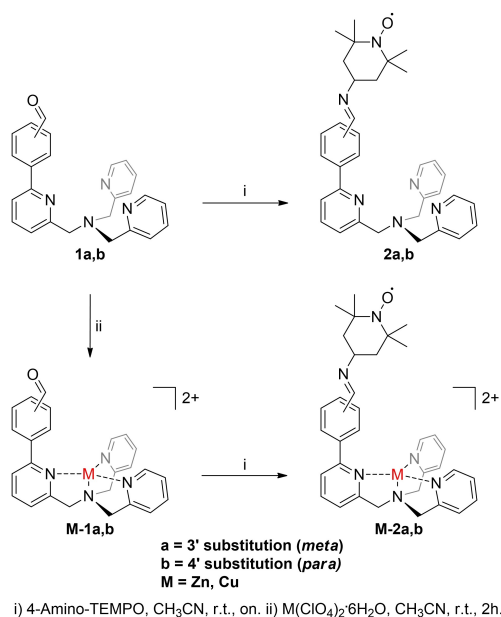
[c] V. Lloveras,<sup>+</sup> J. Veciana, J. Vidal-Gancedo  
Institut de Ciència de Materials de Barcelona (ICMAB-CSIC) and CIBER de  
Bioingeniería, Biomateriales y Nanomedicina, Instituto de Salud Carlos III,  
Campus UAB, E-08193 Bellaterra, Spain  
E-mail: j.vidal@icmab.es

[d] F. A. Scaramuzzo  
Dipartimento di Scienze di Base e Applicate per l'Ingegneria, Università la  
Sapienza, Via del Castro Laurenziano 7, 00161 Roma, Italy

[<sup>+</sup>] These authors contributed equally to the work.

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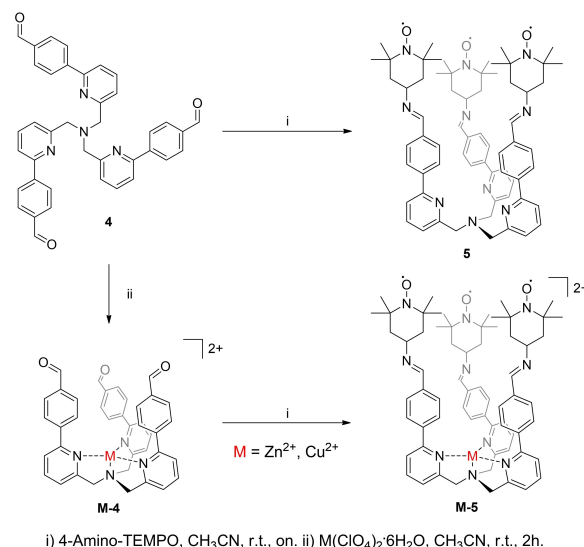
**Scheme 1.** Synthesis of TEMPO-functionalized ligands **2a,b** and their corresponding metal complexes **M-2a,b**. Perchlorate counteranions are removed for clarity.

moiety and the commercially available 4-amino-TEMPO. However, it was not possible to obtain the corresponding metal complexes directly from these ligands: the presence of crystallization water molecules in the perchlorate salts used for the metalation step caused the hydrolysis of the imine bonds. For this reason, the synthesis of the Zn(II) and Cu(II) complexes **M-1a,b** was performed prior to the imine condensation between the aldehyde moiety and the radical 4-amino-TEMPO to obtain the corresponding TEMPO functionalized complexes **M-2a,b**. All the systems were characterized by ESI-MS, FT-IR, EPR and in some cases, <sup>1</sup>H-NMR were recorded.

### Triple TEMPO-Functionalized TPMA Systems

#### Synthesis and Coordination Chemistry

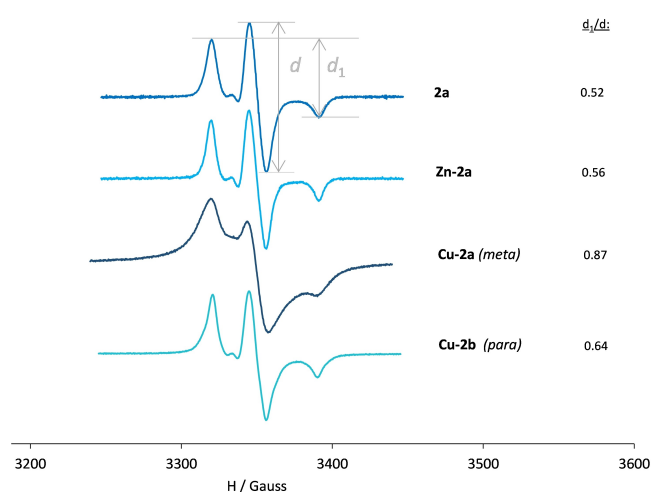
The functionalization of TPMA ligands bearing three aldehyde moieties in *para* position in the pyridine rings started from compound **4** (Scheme 2). As with mono substituted TPMA systems, we first synthesized ligand **5** through an imine condensation between aldehyde moieties and the 4-amino-TEMPO. To obtain the corresponding metal complexes **Cu-5** and **Zn-5**, we performed the same condensation reaction starting from the complexes **M-4**. The resulting compounds **5** and **M-5** were fully characterized by FT-IR, ESI-MS, EPR and <sup>1</sup>H-NMR when significative.



**Scheme 2.** Synthesis of tri-TEMPO-functionalized TPMA systems. Perchlorate counteranions are removed for clarity.

### EPR Spectra of Mono and Triple TEMPO-Functionalized TPMA Systems

The EPR spectra of mono and triple TEMPO-functionalized TPMA systems at 300 K exhibited the three characteristic lines associated to the free TEMPO radical (see the Supporting Information). To determine the possible interaction between the organic radical and the metallic centre, we recorded EPR spectra at low temperature. In frozen solution (120 K), the shape of the spectra change as we are under anisotropic conditions (Figure 1). In such conditions, the CW X-band EPR spectrum is sensitive to the dipole-dipole interaction between neighbouring nitroxides and the radical-metal interaction which significantly modifies the shape of the spectrum, at distances lower



**Figure 1.** EPR spectra of a  $5 \times 10^{-4}$  M solution of ligand **2a**, and complexes **Zn-2a**, **Cu-2a** and **Cu-2b**, at 120 K. **2a** and **Zn-2a** in dichloromethane/toluene (1 : 1) and **Cu-2a/2b** in dichloromethane/toluene (1 : 1): acetonitrile, 8 : 2.

than 2 nm. This effect could be estimated by the empirical ratio of peak heights  $d_{\parallel}/d$  (see SI). This parameter depends on the longitudinal relaxation time  $T_1$  value and it is possible to correlate the value of  $d_{\parallel}/d$  with the radical-radical and radical-metal interaction. The greater the interaction, the greater the  $d_{\parallel}/d$  ratio. Also, the  $d_{\parallel}/d$  parameter can be used to determine the distance between a radical and a paramagnetic transition metal.<sup>[11]</sup>

If there is no interaction between the radical and the metal, the value of  $d_{\parallel}/d$  is the one presented by the isolated TEMPO radical. For example, the radical 4-amino TEMPO in dichloromethane:toluene (1:1),  $5 \times 10^{-4}$  M at 120 K has a  $d_{\parallel}/d$  value of 0.53.<sup>[11d]</sup> A comparison of the  $d_{\parallel}/d$  parameter values, measured in frozen solution at 120 K, of the different compounds presented in this study is reported in Table 1 and the corresponding EPR spectra in Figure 1 and in the Supporting Information.

In the mono-TEMPO series, the  $d_{\parallel}/d$  values of the free ligand **2a** (0,52) it is similar to that of 4-amino-TEMPO and the complex **Zn-2a** is similar too (0,56), which can be explained by the fact that the zinc metal is not paramagnetic, confirming the lack of interaction between the metal and the radical in this system. In the case of the paramagnetic complex **Cu-2a**, the value is much higher (0,87). The role of the solvent must be taken into account: in the latter case, some acetonitrile was used that slightly increases the  $d_{\parallel}/d$  value but even considering this effect, the value is much higher than the ligand, showing the influence of the paramagnetic behavior. If we compare the  $d_{\parallel}/d$  value between **Cu-2a** (0,87) (*meta* position of TEMPO radical) and **Cu-2b** (0,64) (*para* position of TEMPO radical) in the same mixture of solvents (dichloromethane/toluene (1:1):acetonitrile, 8:2) we observed a higher value in the case of *meta* position. This is probably because the TEMPO radical is situated closer to the metallic center in the *meta* position, thus favoring a greater interaction between the metal and the radical.

In the case of the tri-TEMPO series, the compound **5**, which has 3 radicals but is not coordinated with any metal, presents a

$d_{\parallel}/d$  value of 0.54, practically the same than the isolated TEMPO. This indicates that in this configuration there is no interaction between radicals and any increase in  $d_{\parallel}/d$  is due to interaction with metal. In the complex with Zn(II) and with Cu(II) the same mixture of solvents was also used, hence, the solvent's influence was the same. Notably, in the case of **Cu-5**, which is paramagnetic, the  $d_{\parallel}/d$  value was again higher (0,67) than in **Zn-5** (0,59), aligning with the trend observed in the mono-TEMPO series.

## TEMPO Coordinated to the Metallic Center

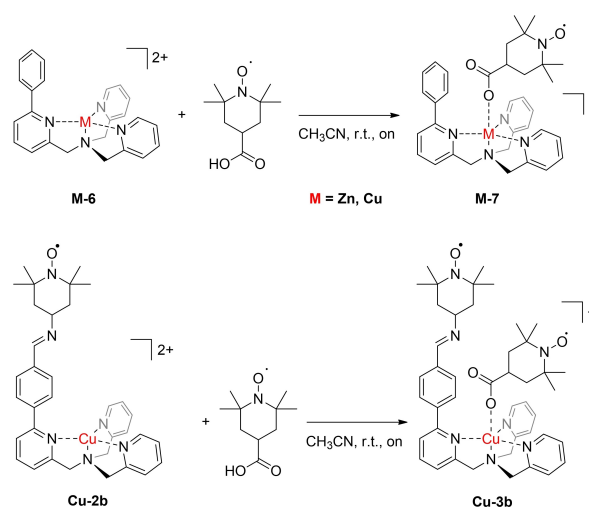
### Synthesis, Coordination Chemistry and EPR Spectra Study

To better understand such metal-radical interaction, different models with a TEMPO radical directly coordinated to the metallic center were synthesized. It is known that carboxylic acids are able to get coordinated to Zn(II) and Cu(II) ions. Consequently, the reactions between the commercial 4-carboxy-TEMPO free radical with three TPMA-metal complexes have been performed (Scheme 3). Complexes **Cu-7** and **Zn-7**, which have been characterized by ESI-MS and EPR, have the radical directly coordinated to the metallic center and no other radicals are covalently linked to the TPMA skeleton. The EPR study in frozen conditions indicated low interaction in both cases (Table 1), although the complex with Cu (**Cu-7**) (0,58) also showed slightly larger  $d_{\parallel}/d$  value than the same one with Zn (**Zn-7**) (0,52). This means that even if the radical is directly coordinated to the metallic center, no interactions or very low ones between them are observed in this geometry.

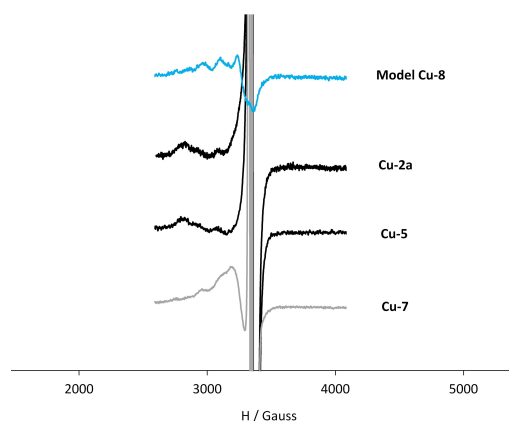
In order to determine the contribution of a covalently attached TEMPO radical, we synthesized another model compound with both a TEMPO radical coordinated directly to the metallic center and another one covalently attached to the TPMA structure (**Cu-3b**) and measured the  $d_{\parallel}/d$  parameter. The value obtained was slightly higher than the previous ones

**Table 1.** Reported  $d_{\parallel}/d$  parameter values of the different compounds reported in this study.

Compounds	Solvent	$d_{\parallel}/d$
Mono-TEMPO Series		
<b>2a</b>	No ACN	0.52
<b>Zn-2a</b>	No ACN	0.56
<b>Cu-2a (meta)</b>	ACN	0.87
<b>Cu-2b (para)</b>	ACN	0.64
Tri-TEMPO Series		
<b>5</b>	No ACN	0.54
<b>Zn-5</b>	ACN	0.59
<b>Cu-5</b>	ACN	0.67
TEMPO-Metal series		
<b>Zn-7</b>	ACN	0.52
<b>Cu-7</b>	ACN	0.58
<b>Cu-3b</b>	ACN	0.66



**Scheme 3.** Synthesis of metal complexes **Zn-7**, **Cu-7** and **Cu-3b**. Perchlorate counteranions are removed for clarity.



**Figure 2.** EPR spectra of a  $10^{-3}$  M solution of complexes **Cu-2a**, **Cu-5** and **Cu-7** in dichloromethane/toluene (1:1) with 20% of ACN.

suggesting that the TEMPO radicals covalently attached to the ligand exerted a greater influence on the metal-radical interaction.

### EPR Spectra of the Cu(II) Region

We also recorded the Cu(II) region of the EPR spectra of complexes **Cu-2a**, **Cu-5** and **Cu-7** in frozen conditions (Figure 2). Moreover, in order to compare their corresponding EPR signal with a Cu(II) reference, we designed a model compound, **Cu-8**, displaying the same structure of complex **Cu-5** but bearing phenyl groups instead of TEMPO radicals (Figure 2). The EPR spectra at 300 and 120 K of **Cu-8** are depicted in the Supporting Information. From the comparison between the EPR spectra of complexes **Cu-2a**, **Cu-5** and **Cu-7** and the model **Cu-8** at 120 K (Figure 2), it is possible to observe that the Cu(II) signal got broadened in **Cu-2a** and **Cu-5** complexes due to the presence of TEMPO radicals, which is another proof of certain metal-radical interaction.<sup>[12]</sup> However, the Cu(II) signal got almost unaltered in the case of **Cu-7**, which is in agreement with the previous observations made from the corresponding  $d_{\parallel}/d_{\perp}$  parameter study.

### Conclusions

Herein we report the synthesis of a new family of stable radical-containing polytopic ligands and the study of their corresponding metal complexes. This had offered the possibility to study their emerging properties, arising from the presence of two different kinds of spin carriers, the metal ion and the organic radical. We have observed certain metal-radical interaction only when the metallic center is paramagnetic, Cu(II). This interaction is notably weaker when the radical coordinates directly to the metal, but becomes more pronounced when the radical is covalently attached, particularly in the *meta* molecular arrangement.

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### Conflict of Interests

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** TEMPO · Tetradentate ligands · EPR · Radical interaction · TPMA

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