

# 1-Phenyl-3-(pyrid-2-yl)benzo[*e*][1,2,4]triazinyl: The First “Blatter Radical” for Coordination Chemistry

Ian S. Morgan,<sup>\*,†</sup> Anssi Peuronen,<sup>†</sup> Mikko M. Hänninen,<sup>†</sup> Robert W. Reed,<sup>‡</sup> Rodolphe Clérac,<sup>§,⊥</sup> and Heikki M. Tuononen<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry, University of Jyväskylä, P.O. Box 35, FI-40014 Jyväskylä, Finland

<sup>‡</sup>Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada

<sup>§</sup>CNRS, CRPP, UPR 8641, F-33600 Pessac, France

<sup>⊥</sup>Université Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France

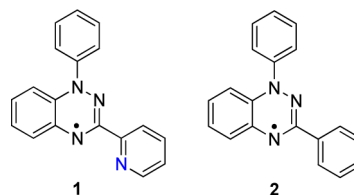
## Supporting Information

**ABSTRACT:** A neutral air- and moisture-stable N,N'-chelating radical ligand, 1-phenyl-3-(pyrid-2-yl)benzo[*e*][1,2,4]triazinyl (**1**) was synthesized and characterized by electron paramagnetic resonance spectroscopy, X-ray crystallography, and magnetic measurements. Subsequent reaction of **1** with Cu(hfac)<sub>2</sub>·2H<sub>2</sub>O (hfac = hexafluoroacetylacetonate) under ambient conditions afforded the coordination complex Cu(**1**)(hfac)<sub>2</sub> in which the radical binds to the metal in a bidentate fashion. Magnetic susceptibility data collected from 1.8 to 300 K indicate a strong ferromagnetic metal-radical interaction in the complex and weak antiferromagnetic radical...radical interactions between the Cu(**1**)(hfac)<sub>2</sub> units. Detailed computational investigations support this assignment. Radical **1** is a new addition to the growing library of 1,2,4-triazinyl radicals and the first member of this family of paramagnetic species synthesized specifically for coordination purposes.

New magnetic materials are becoming increasingly important as technology advances toward the ultimate size barrier, the molecular limit. A quintessential requirement for the development of “molecular spin science” is the ability to rationally manipulate the magnetic couplings within these materials. One possible technique is to utilize the metal-radical approach in which organic radical ligands are used to mediate the magnetic coupling between paramagnetic metal centers.<sup>1</sup> While there exists a plethora of open-shell ligands that can coordinate to metals (e.g., semiquinones,<sup>2,3</sup> nitroxides,<sup>4</sup> thiazyls,<sup>5,6</sup> and verdazyls<sup>7,8</sup>), many of them are not air- and moisture-stable and, hence, cannot be used as building blocks for practical magnetic materials.<sup>9,10</sup> In this contribution, we report the synthesis of a new stable coordinating radical, 1-phenyl-3-(pyrid-2-yl)benzo[*e*][1,2,4]triazinyl (**1**), and demonstrate its desired coordinating properties via complete characterization of its copper(II) complex by experimental and theoretical methods.

Blatter's radical (**2**), developed in 1968, has received limited attention despite its stability toward both air and water.<sup>11</sup> It has been cocrystallized with tetracyanoquinodimethane to make pressure-sensitive charge-transfer complexes,<sup>12</sup> while its derivatives have been extensively studied for their magnetic

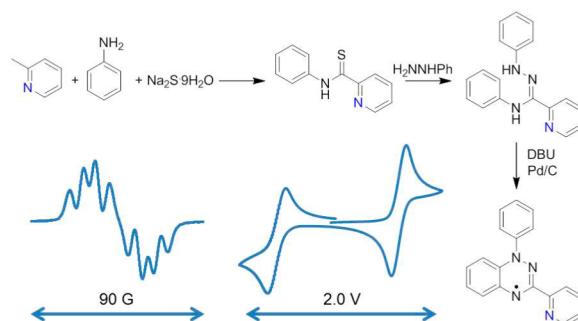
behavior.<sup>13–18</sup> Curiously, until now, no coordination attempts of this radical or modifications of the radical architecture for coordination purposes have been reported.



The preparation of **1** begins with formation of the corresponding pyridylthioamide species via the reaction of picoline, sodium sulfide, and aniline, followed by a reaction with phenyl hydrazine to afford pyridyl amidrazone and H<sub>2</sub>S (see S1 in the Supporting Information, SI). Ring closure and oxidation of the purified amidrazone can then be accomplished using a combination of Pd/C and 1,8-diazabicycloundec-7-ene in air.<sup>13</sup> The purity of the product is ensured using column chromatography followed by recrystallization. None of the above steps requires any specific precautions, and **1** can be stored under ambient conditions, as reported for other derivatives of **2**.<sup>19</sup>

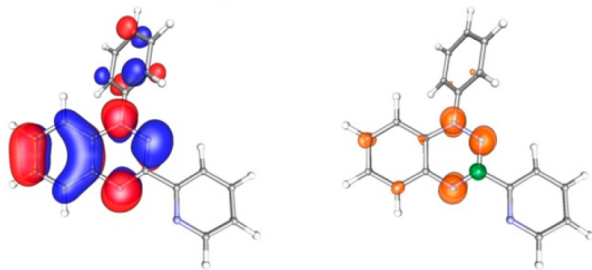
The X-band electron paramagnetic resonance (EPR) spectrum of **1** in CH<sub>2</sub>Cl<sub>2</sub> (Scheme 1 and S2 in the SI) shows a septet pattern consistent with the coupling of the unpaired electron to

**Scheme 1. Synthesis of the radical **1** along with its EPR and CV signatures (in CH<sub>2</sub>Cl<sub>2</sub>)**



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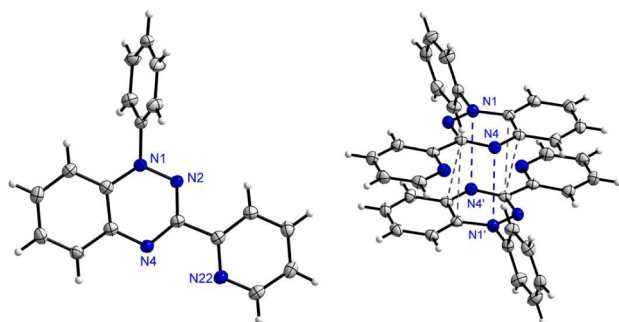
three distinct nitrogen atoms ( $g = 2.0040$ ,  $a_{\text{N1}} = 6.43$  G,  $a_{\text{N2}} = 4.29$  G,  $a_{\text{N3}} = 3.92$  G, and  $Iw = 2.01$  G). The EPR signature of **1** can be easily understood on the basis of density functional theory (DFT) calculations (S6 in the SI). While there are four nitrogen atoms in the molecule, the singly occupied molecular orbital (SOMO) of **1** possesses a node on the carbon atom bearing the pyridyl substituent (Figure 1), as calculated for other 1,2,4-



**Figure 1.** Isosurface plots of the SOMO (left) and spin density (right) of **1**.

triazinyls.<sup>19</sup> The spin density of **1** is absent on the pyridyl group (and thus N22), while it shows an excess  $\alpha$  density on the fused triazine and benzo rings, with a large percentage at the two nitrogen atoms N2 and N4, which could coordinate to metal centers. Cyclic voltammetry experiments of **1** in  $\text{CH}_2\text{Cl}_2$  (Scheme 1 and S3 in the SI) indicate reversible  $0/1+$  and  $1-/0$  couples with  $E_{1/2} = 6$  and  $-1140$  mV and  $\Delta E_{\text{pp}} = 140$  and  $160$  mV, respectively (vs standard calomel electrode).<sup>20</sup>

Crystals of **1** belong to monoclinic space group  $P2_1/n$ . There are four molecules per unit cell that form radical pairs with close  $\text{N}\cdots\text{N}$  [3.215(1) Å] and  $\text{C}\cdots\text{C}$  [3.294(2) Å] contacts (Figure 2).

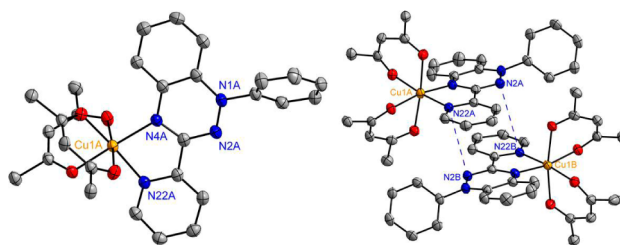


**Figure 2.** Single-crystal X-ray structure of **1** (left) and its packing to  $\pi$  dimers in the solid state at 123 K (right). Thermal ellipsoids are drawn at the 50% probability level.

Magnetic susceptibility measurements performed on a polycrystalline sample of **1** indicate that the radical pairs are strongly antiferromagnetically coupled and are essentially diamagnetic below 100 K (S5 in the SI). On the basis of radical dimer topology, this system can be viewed as an  $S = 1/2$  spin dimer described by the isotropic Heisenberg spin Hamiltonian  $H = -2J\hat{S}_1\hat{S}_2$ , where  $J$  is the radical–radical magnetic interaction. In the weak-field approximation, the analytical expression of magnetic susceptibility can be estimated by applying the van Vleck equation.<sup>21</sup> The experimental data are well fitted to this model with  $g = 2.0(1)$  and  $J/k_B = -412(3)$  K, while the broken-symmetry DFT calculations predict  $J = -335$  K (S6 in the SI).

After synthesis and characterization of the new radical ligand **1**, its coordinating properties with paramagnetic metal centers were put to the fore. Owing to the intrinsic azaphilic nature of

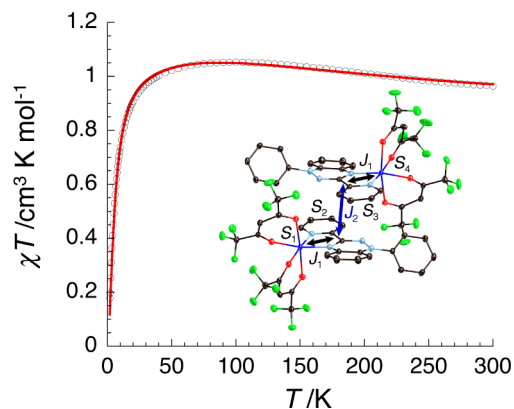
copper(II) salts and the stability of **1** toward water, we opted to use copper(II) hexafluoroacetylacetonate dihydrate,  $\text{Cu}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$ , as the starting material. Thus, the complex  $\text{Cu}(\text{I})(\text{hfac})_2$  (**3**) was prepared by treating **1** with  $\text{Cu}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$  in  $\text{CH}_2\text{Cl}_2$  under ambient conditions. Crystalline material of the product was grown by slow diffusion with pentane to afford large purple blocks. The single-crystal X-ray structure of **3** displays an octahedral copper(II) center with a typical Jahn–Teller distorted geometry (Figure 3). The radical binds to the metal in a bipyridine-like fashion, as designed, with a nearly planar coordination pocket.



**Figure 3.** Single-crystal X-ray structure of **3** (left) and its packing to weakly interacting  $\pi$  dimers in the solid state at 123 K (right). Fluorine and hydrogen atoms are removed for clarity, and thermal ellipsoids are drawn at the 50% probability level.

Complex **3** exhibits a reversible single crystal-to-single crystal phase transition, whereupon cooling the sample from 298 to 123 K results in an approximate doubling of the crystallographic  $a$  axis. This temperature-related phase transition is accompanied by resolution of the positions of the  $\text{CF}_3$  groups as well as minor (ca. 0.1 Å) strengthening of the radical–radical interaction. It should be noted that, in contrast to **1**, complex **3** is unable to effectively  $\pi$ -stack in the solid state because of the steric bulk of the hfac ligands. Consequently, the  $\text{Cu}(\text{I})(\text{hfac})_2$  units interact very weakly in the crystal structure even at 123 K [closest  $\text{N}\cdots\text{N}$  distance of 3.745(2) Å in **3** compared to 3.215(1) Å for **1**], and the observed phase transition has no apparent effect on the magnetic properties of **3** [cf. related “breathing” crystals of composition  $\text{Cu}(\text{L}^R)(\text{hfac})_2$ ].<sup>22</sup>

The magnetic properties of **3** were investigated over the temperature range from 1.8 to 300 K with an applied field of 1000 Oe (Figure 4). At 300 K, the  $\chi T$  value is  $0.96 \text{ cm}^3 \text{ K mol}^{-1}$ , with



**Figure 4.** Temperature dependence of the  $\chi T$  product for **3** at 1000 Oe [with  $\chi$  defined as the molar magnetic susceptibility equal to  $M/H$  per mole of  $\text{Cu}(\text{I})(\text{hfac})_2$ ]; measured data (black circles); best fit (red line). Inset: schematic view of the spin interaction topology in **3**.

an increase to  $1.05 \text{ cm}^3 \text{ K mol}^{-1}$  when the temperature is lowered to 100 K. This thermal behavior can be attributed to ferromagnetic coupling between the radical ligand and the copper(II) spin. Upon further cooling, the  $\chi T$  product decreases to  $0.2 \text{ cm}^3 \text{ K mol}^{-1}$ , which is consistent with additional antiferromagnetic interactions likely between the radical spins of the neighboring  $\text{Cu(1)(hfac)}_2$  complexes. The magnetic data were fitted to the theoretical susceptibility calculated in the low-field approximation using the isotropic Heisenberg spin Hamiltonian  $H = -2J_1(S_1 \cdot S_2 + S_3 \cdot S_4) - 2J_2(S_2 \cdot S_3)$  and considering the presence of both Cu–radical ( $J_1$ ) and radical–radical ( $J_2$ ) interactions (Figure 4, inset, and S5 in the SI).<sup>23</sup> The model fits extremely well to the experimental data (Figure 4) and accurately gives the relevant magnetic parameters:  $g = 2.10(5)$ ,  $J_1/k_B = +144(7) \text{ K}$ , and  $J_2/k_B = -9.5(5) \text{ K}$ . This analysis demonstrates the  $S = 1$  ground state of the  $\text{Cu(1)(hfac)}_2$  complex ( $J_1$ ) and coupling of the pairs of these complexes to give an overall  $S = 0$  state ( $J_2$ ). We note that the Cu–radical magnetic exchange interaction is larger in **3** than in analogous verdazyl-copper(hfac) complexes,<sup>24</sup> possibly because of Jahn–Teller distortion of the bonds to the coordinated verdazyl ligand.

Both the  $J_1$  and  $J_2$  interactions observed in **3** can be rationalized via the orbital-symmetry approach (S6 in the SI). The ferromagnetic coupling between the copper(II) spin and the coordinated radical originates from the orthogonality of  $d_{x^2-y^2}$  and  $p_\pi$  magnetic orbitals for the metal ion and the ligand, respectively. Similarly, the antiferromagnetic coupling between radicals in the  $\text{Cu(1)(hfac)}_2$  pairs is mediated through a small overlap of the two radical-centered magnetic orbitals. In agreement with the above description, broken-symmetry DFT calculations predicted also the nature of  $J_1$  and  $J_2$  (ferro- vs antiferromagnetic) for **3** (S6 in the SI). Although calculations slightly underestimate the coupling strengths, the theoretical values ( $+121$  and  $-1.11 \text{ K}$ , respectively, at  $293 \text{ K}$ ) are in good agreement with the experimental data and unequivocally show that the metal–radical interaction is considerably stronger than the radical–radical coupling.

In conclusion, a new neutral open-shell ligand, 1-phenyl-3-(pyrid-2-yl)benzo[*e*][1,2,4]triazinyl, is shown to be completely air- and water-stable and capable of chelating metal ions. The radical **1** is an important addition to the limited list of stable paramagnetic ligands that can be handled under ambient conditions without any specific precautions. The desirable coordinating abilities of **1** were demonstrated via synthesis and characterization of the complex  $\text{Cu(1)(hfac)}_2$ , the first example of metal coordination using a 1,2,4-benzotriazinyl-based architecture. The bipyridine-like  $N,N'$ -chelating pocket ensures a wide coordination chemistry for **1**, the exploration of which is currently underway in our group. The results of these investigations, as well as further modifications to enhance the metal-binding abilities of **1**, will be reported in future publications.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Experimental and computational details, X-ray crystallographic and magnetic data of **1** and **3**, and EPR spectrum and cyclic voltammogram of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: [ian.s.morgan@jyu.fi](mailto:ian.s.morgan@jyu.fi).

\*E-mail: [heikki.m.tuononen@jyu.fi](mailto:heikki.m.tuononen@jyu.fi).

## Notes

The authors declare no competing financial interest.

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