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Year: 2014

Version:

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

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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 EPR spectroscopy, X-ray crystallography, and magnetic measurements. Subsequent reaction of **1** with $Cu(hfac)_2 \cdot 2H_2O$ (hfac = hexafluoroacetylacetonate) under ambient conditions afforded the coordination complex $Cu(\mathbf{1})(hfac)_2$ in which the radical binds to the metal in bidentate fashion. Magnetic susceptibility data collected from 1.8 to 300 K indicates a strong ferromagnetic metal-radical interaction in the complex and weak antiferromagnetic radical···radical interactions between the $Cu(\mathbf{1})(hfac)_2$ units. Detailed computational calculations 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 towards 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.[1] While there exists a plethora of open shell ligands that can coordinate to metals (*e.g.* semiquinones,[2,3] nitroxides,[4] thiazyls,[5,6] and verdazyls[7,8]), many of them are not air and moisture stable, and hence, cannot be used as building blocks for practical magnetic materials.[9,10] 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 towards both air and water.[11] It has been co-crystallized with tetracyanoquinodimethane to make pressure-sensitive charge transfer complexes[12] while its derivatives have been extensively studied for their magnetic behavior.[13-18] Curiously, until now, no coordination attempts of this radical nor modifications of the radical architecture for coordination purposes have been reported.
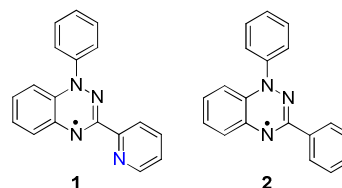
The preparation of **1** begins with the formation of the corresponding pyridyl-thioamide species *via* reaction of picoline, sodium sulfide, and aniline, followed by a reaction with phenyl hydrazine to afford pyridyl-amidrazone and H_2S (ESI-S1). Ring closure and oxidation of the purified amidrazone can then be accomplished using a combination of Pd/C and 1,8-diazabicycloundec-7-ene in air.[13] The purity of the product is ensured using column chromatography followed by recrystallization. None of the above steps require any specific precautions and **1** can be stored under ambient conditions as reported for other derivatives of **2**.[19]

Scheme 1. Synthesis of the radical **1** along with its EPR and CV signatures (in CH_2Cl_2).
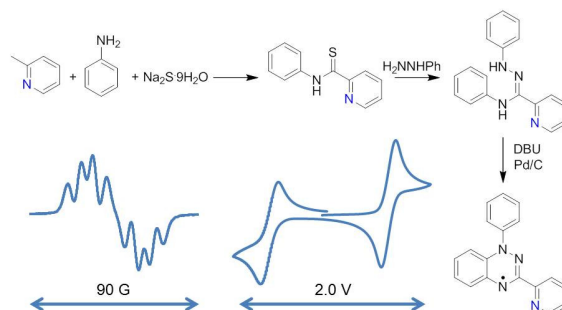
The X-band EPR spectrum of **1** in CH_2Cl_2 (Scheme 1; ESI-S2) shows a septet pattern consistent with the coupling of the unpaired electron to three distinct nitrogen atoms (g = 2.0040, a_{N_1} = 6.43 G, a_{N_2} = 4.29 G, and a_{N_3} = 3.92 G, and *l.w.* = 2.01

G). The EPR signature of **1** can be easily understood on the basis of density functional theory (DFT) calculations (ESI-S6). 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 with other 1,2,4-triazinyls.[19] 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 that could coordinate to metal centers. Cyclic voltammetry experiments of **1** in CH_2Cl_2 (Scheme 1; ESI-S3) indicate reversible 0/+1 and -1/0 couples with $E_{1/2}$ = 6 and -1140 mV and ΔE_{pp} = 140 and 160 mV, respectively (*vs.* standard calomel electrode).[20]
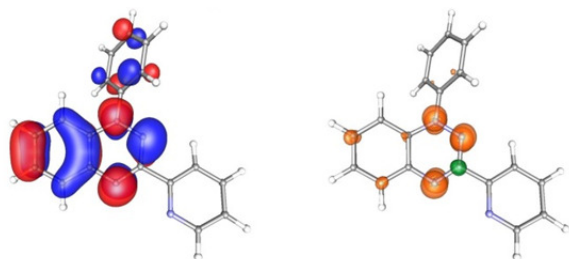

Figure 1. Isosurface plots of the singly occupied molecular orbital (SOMO; left) and spin density (right) of **1**.
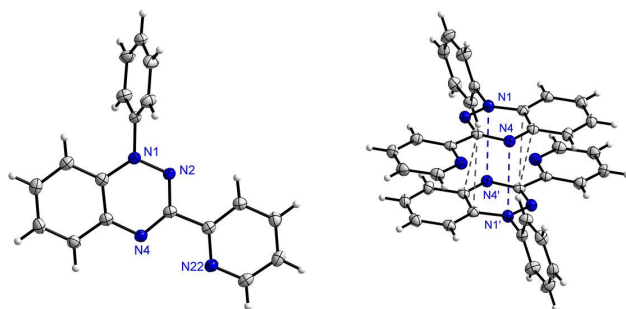

Figure 2. Single crystal X-ray structure of **1** (left) and its packing to π-dimers in the solid state at 123 K (right). Thermal ellipsoids are drawn at the 50% probability level.

Crystals of **1** belong to monoclinic space group $P2_1/n$. There are four molecules per unit cell which form radical pairs with close N···N (3.215(1) Å) and C···C (3.294(2) Å) contacts (Figure 2). 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 (ESI-S5). On the basis of the radical dimer topology, this system can be viewed as an S = 1/2 spin dimer described by the isotropic Heisenberg spin Hamiltonian $H = -2JS_1S_2$, where J is the radical···radical magnetic interaction. In the weak field approximation, the analytical expression of magnetic susceptibility can be estimated applying the van Vleck equation.[21] 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 (ESI-S6).

After the 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 azaphillic

nature of copper(II) salts and the stability of **1** towards water, we opted to use copper(II)hexafluoroacetylacetonate dihydrate, $Cu(hfac)_2 \cdot 2H_2O$, as the starting material. Thus, the complex $Cu(1)(hfac)_2$ (**3**) was prepared by treating **1** with $Cu(hfac)_2 \cdot 2H_2O$ in CH_2Cl_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.
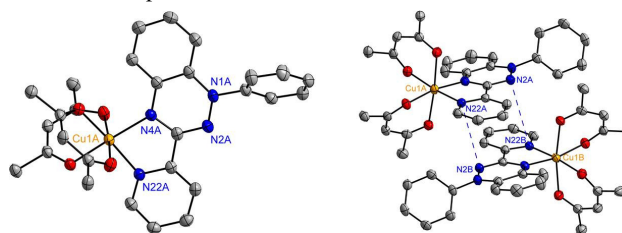

Figure 3. Single crystal X-ray structure of **3** (left) and its packing to weakly interacting π-dimers in the solid state at 123 K (right). Fluorine and hydrogen atoms are removed for clarity and thermal ellipsoids are drawn at the 50% probability level.

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 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 π-stack in the solid state due to the steric bulk of the hfac ligands. Consequently, the $Cu(1)(hfac)_2$ units interact very weakly in the crystal structure even at 123 K (closest N···N distance of 3.745(2) Å in **3**, *cf.* 3.215(1) Å for **1**) and the observed phase transition has no apparent effect to the magnetic properties of **3** (*cf.* related 'breathing' crystals of the composition $Cu(L^R)(hfac)_2$.[22]

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 χT value is 0.96 cm^3 $Kmol^{-1}$, with an increase to 1.05 cm^3 K mol^{-1} when lowering the temperature to 100 K. This thermal behavior can be attributed to ferromagnetic coupling between the radical ligand and the Cu(II) spin. Upon further cooling, the χT product decreases to 0.2 cm^3 K mol^{-1}, which is consistent with additional antiferromagnetic interactions likely between the radical spins of the neighboring $Cu(1)(hfac)_2$ 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; ESI-S5).[23] 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) K, and J_2/k_B = -9.5(5) K. This analysis demonstrates the S = 1 ground state of the $Cu(1)(hfac)_2$ complex (J_1) and coupling of the pairs of these complexes to give an overall S = 0 state (J_2).

We note that the copper-radical magnetic exchange interaction is larger in **3** than in analogous verdazyl-copper(hfac) complexes,[24] possibly due to the Jahn-Teller distortion of the bonds to the coordinated verdazyl ligand.
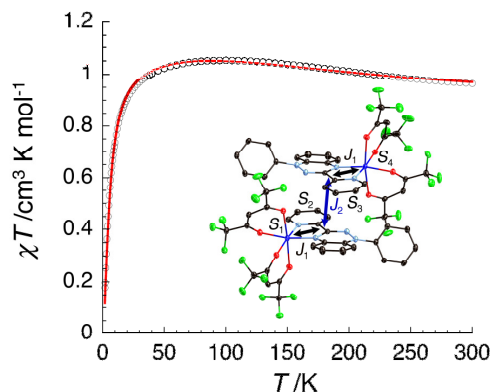

Figure 4. Temperature dependence of the χT product for **3** at 1000 Oe (with χ defined as molar magnetic susceptibility equal to M/H per mole of Cu(**1**)(hfac)$_2$); measured data (black circles) and best fit (red line). Inset: schematic view of the spin interaction topology in **3**.

Both the J_1 and J_2 interactions observed in **3** can be rationalized *via* orbital-symmetry approach (ESI-S6). The ferromagnetic coupling between the Cu(II) spin and the coordinated radical originates from the orthogonality of $d_{x^2-y^2}$ and p_π magnetic orbitals for the metal ion and the ligand, respectively. Similarly, the antiferromagnetic coupling between the radicals in Cu(**1**)(hfac)$_2$ pairs is mediated through 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.* antiferro-magnetic) for **3** (ESI-S6). Although the calculations slightly underestimate coupling strengths, the theoretical values (+121 and -1.11 K, respectively, at 293 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 Cu(**1**)(hfac)$_2$, the first example of accomplishing 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.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

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3