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## A stable open-shell redox active ditopic ligand

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Herein we describe the synthesis, structure and electronic properties of an unusual redox-active ditopic ligand with a stable open-shell configuration. This stable phenoxyl radical features intense and very low energy electronic transitions in the near infrared (NIR) part of the spectrum and is structurally set up to strongly spin couple coordinated transition metal ions in [2x2] grid-type structures.

Redox-active bridging ligands that feature stable open-shell configurations have been shown to be very effective spin coupling units for the production of high-spin ground state complexes.<sup>1-3</sup> Often and under the right conditions, complexes containing paramagnetic bridging ligands produce excellent single molecule magnets (SMMs) with high blocking temperatures and display significantly higher thermal hysteresis temperatures.<sup>4-6</sup> The very strong spin coupling in these complexes serves to "isolate" the spin ground state from excited states resulting in higher hysteresis temperatures. So far the synthetically accessible paramagnetic bridging ligands have allowed for the production of mostly bimetallic complexes. In order to generate higher spin states there is a need to design and synthesize open-shell ligands that are capable of binding multiple metal ions in large coordination arrays. Polytopic ligands<sup>7-9</sup> are an obvious target in this regard and a large number of these have been synthesized, but very few feature a stable open-shell structure.<sup>10-12</sup> While fascinating polynuclear grid-type complexes have been reported with very large arrays of metal ions included in the structure, the magnetic exchange coupling between paramagnetic metal ions is always very weak superexchange through the diamagnetic bridge. We have identified a synthetic approach to produce polytopic paramagnetic bridging ligands and herein report the synthesis and properties of 3 (BAQP). BAQP, a uniquely stable phenoxyl radical, features two, contiguous NNO donor sites and should be capable of binding two metal ions bridged by the central spin-density rich O atom in [2x2] grid-type complexes. BAQP represents the first crystallized phenoxyl radical lacking tert-butyl substituents flanking the C-O bond.

**BAOP** is synthesized in five steps starting from commercially available 4-tert-butylphenol (Scheme 1). Iodination of 4-tertbutylphenol followed by protection with methyl iodide produced 2,6-di-iodo-4-tert-butylanisole<sup>13</sup>, which was cross-coupled to excess 8-aminoquinoline using Buchwald-Hartwig C-N bond formation chemistry<sup>14</sup> to produce **1**. We anticipated that deprotection of **1** with BBr<sub>3</sub> would yield phenol **2**, however, we were unable to acquire a <sup>1</sup>H NMR spectrum of the deprotection product at room temperature. High-resolution mass spectrometry (ESI and EI) and elemental analysis indicated a molecular formula of this product consistent with the structure of 2 as shown in Scheme 1. However, in the liquid chromatogram of 2, we quickly see one peak change to two peaks; the new peak that grows in has the same m/z as the original peak and so is likely an isomer of 2. Upon cooling a  $d^{\delta}$ -toluene solution of 2 down to 235 K, an <sup>1</sup>H NMR spectrum of 2 interpreted with the phenol structure described in Scheme 1 is acquired (Figure S13<sup>†</sup>), which disappears if the solution is warmed back to room temperature. In the 235 K spectrum, the OH resonance is observed at 10.03 ppm and all 14 aromatic, 2 NH and 9 tert-butyl protons are accounted for (at this temperature no coupling could be resolved but the correct number of absorptions with appropriate integration are observed). These data suggest that an equilibrium exists between compound 2, in the form of the diamagnetic phenol product, with an unknown paramagnetic species; the diamagnetic phenol is the stable product at low temperature, and the paramagnetic isomer is dominant at elevated temperatures. All of our spectroscopic data indicate that this paramagnetic species bears the same molecular formula as phenol 2 and is not a product from the aerial oxidation of 2, which we originally hypothesized. The UV-vis-NIR spectrum of 2 at room temperature (Figure S10<sup>†</sup>) is markedly different from the spectrum of the oxidized product, 3 BAQP (Figure 4, described later). Further support for the presence of this unusual equilibrium was provided by EPR spectroscopy. An EPR spectrum was obtained in toluene solution for 2 at room temperature, which disappears when the solution is frozen but reappears on warming (Figure S14<sup>†</sup>). We are currently attempting to acquire single crystal X-ray data to identify the structure of the paramagnetic component of this equilibrium.

Dalton Transactions Accepted Manuscript

We anticipated facile oxidation of **2** (which is more precisely an equilibrium mixture of **2** with a paramagnetic product bearing the same molecular formula as **2**) and expected a three-electron oxidation (including each NH and the OH) to produce an "aminyl" type radical as shown in Figure 1. Oxidation with NaIO<sub>4</sub> in methanol immediately produced a forest green precipitate, which was isolated and characterized. However, the high-resolution mass spectrum indicated a product with a mass-to-charge ratio two units higher than anticipated and features present in the FT-IR spectrum were consistent with an NH stretch.



Scheme 1. Synthesis of **3** (**BAQP**). Note that **2** is actually an equilibrium mixture of **2** with a paramagnetic isomer that is not yet structurally characterized.



Fig.1. Anticipated "aminyl" radical following three-electron oxidation of 2.

From a THF solution we were fortunate to obtain X-ray diffraction quality crystals of **3** by slow evaporation after about 3 months. We note that the spectroscopic properties of the single crystals are identical with the precipitated powder. The molecular structure of **3** is shown in Figure 2 and indeed indicates the presence of intact NH groups. The central OH group is the only fragment touched in the oxidation and the structure is that of a substituted phenoxyl radical. **3** is a very rare example of a structurally characterized phenoxyl radical.<sup>15,16</sup>



Fig.2. Molecular structure of **BAQP 3** (displacement ellipsoids at 30% probability) with THF solvent molecule excluded for clarity. Relevant bond distances (Å) and

angles(°) [with standard uncertainties (su) in brackets]: O(1)-C(1), 1.256(2); N(1)-C(2), 1.374(2); N(1)-C(7), 1.387(2); N(2)-C(6), 1.374(2); N(2)-C(16), 1.383(2); C(1)-C(2), 1.457(3); C(2)-C(3), 1.380(3); C(3)-C(4), 1.400(3); C(4)-C(5), 1.405(3); C(5)-C(6), 1.377(3); C(4)-C(25), 1.533(3). C(2)-N(1)-C(7), 131.28(17); C(6)-N(2)-C(16), 132.29(17); O(1)-C(1)-C(6), 121.64(16); O(1)-C(1)-C(2), 116.80(16); C(2)-C(3)-C(1), 120.33(17); C(2)-C(3)-C(4), 121.04(17); C(3)-C(4)-C(25), 120.15(17); C(3)-C(4)-C(25), 127.25(17); N(2)-C(6)-C(1), 112.19(16); C(5)-C(4), 120.56(16). Relevant crystal data and structure refinement parameters are provided in the Supporting Information (Table S1†).

In the molecular structure the metrical parameters of the flanking aminoquinoline rings are unremarkable and typical. However, the C-C bond distances around the central ring clearly show its nonbenzenoid nature; C(1)-C(6) and C(1)-C(2) distances are on the order of single bonds and C(2)-C(3), C(3)-C(4), C(4)-C(5), C(5)-C(6) distances are typical benzenoid length. The C(1)-O(1) distance is between that typically observed for C-O single or double bonds and in line with the distance measured in the two other known monomeric phenoxyl radical crystals.<sup>15,16</sup> The molecular packing of **3** is shown in Figure S1<sup>†</sup>. Very short  $\pi$ -contacts are evident between head-over-tail stacked molecules in the *ac* plane. The distance between O(1) and C(4) among adjacent molecules is 2.838 Å.

Other evidence for the open-shell nature of **3** is provided by electron paramagnetic resonance (EPR) spectroscopy (Figure 3). Powder and solution (CH<sub>2</sub>Cl<sub>2</sub>) EPR spectra are similar for **3** and display a broad signal centered at around 3345 G (g = 2.004). No hyperfine coupling was resolved in the solution spectrum, which was deoxygenated and dilute. The solution EPR data were recorded over a range of temperatures (Figure S4<sup>†</sup>), which provided very similar spectra down to 20 K where a large increase in signal intensity was observed. This signal intensity increase at 20 K is unusual and is a feature of **3** that we are continuing to investigate.



Fig. 3. Powder (top) and solution (CH<sub>2</sub>Cl<sub>2</sub>, 1 mM) EPR spectra of **3** at 298 K. Frequency = 9.38 GHz, microwave power = 2 mW, modulation amplitude = 0.5 G.

The UV-visible-NIR spectrum of **3** was recorded in  $CH_2Cl_2$  and is shown in Figure 3. The higher energy portion of the spectrum is very different from that of 2 and a broad and intense absorption centered at unusually low energy (1129 nm) was also observed. This low energy band is assigned to the BHOMO-to-BLUMO transition in 3 from time-dependent density functional theory calculations (TD-DFT). The energy of this transition is much lower than in other reported phenoxyl radicals, which typically exhibit absorptions between 600-800 nm.<sup>17</sup> The large flanking aminoquinoline substituents result in extensive  $\pi$ -delocalization, which is reflected in the HOMO/LUMO composition (Figure S7 and S8<sup>+</sup>) and the dramatic red shifted absorption energy. A low potential (-0.4 V vs Ag/AgCl in DMF) reversible cathodic process was observed in the cyclic voltammogram of 3, which we assign to the reduction of the radical (Figures S5 and S6<sup>†</sup>). Anodic scans feature low potential quasi-reversible waves centered at about 0.4 V (vs Ag/AgCl) and higher potential irreversible processes. The lower potential wave is

**Journal Name** 

likely oxidation of one NH to produce an orthoquinone-type structure.



Fig. 4. UV-vis-NIR spectrum of **3** (green trace) in THF (298 K). Black bars are TDDFT calculated transitions (UB3LYP/def2-tzvp).

To calculate the spin-density distribution in 3 we optimized the geometry [UB3LYP/6-31G(d,p)] of the radical starting from the coordinates obtained from X-ray crystallography. The calculated structure is in good agreement to the X-ray structure. A single point energy calculation (UB3LYP/def2-tzvp) was carried out on the optimized structure and the resulting spin-density distribution is shown in Figure 5. The calculated positive ( $\alpha$ ) spin-density is concentrated at O(1) as well on the ortho [C(6) and C(2)], para [C(4)] and ipso [C(1)] carbon atoms of the central ring, with smaller components on N(2), N(1) and very small quantities on the flanking quinoline rings. The spin density on these N atoms did not result in resolved hyperfine splitting in the EPR spectrum of 3 in solution. Smaller amounts of negative ( $\beta$ ) spin-density are localized on *meta* carbon atoms C(5) and C(3). This is the first example of a crystallized phenoxyl radical with substituents other than tert-butyl groups at C(6) and C(2). The large spin densities on N, N, O donor atoms is promising for the observation of strong magnetic exchange coupling in polynuclear complexes.



Fig. 5. Spin-density distribution in **3** (UB3LYP/def2-tzvp).  $\alpha$ - or  $\beta$ -spin density is red or blue, respectively. Iso-value is 0.004.

### Conclusions

In summary we have reported the synthesis, structure and electronic properties of a new open-shell ditopic ligand **3** (BAQP). This represents only the third structurally characterized phenoxyl radical and the first with non-*tert*-butyl substituents at C2 and C6. This radical absorbs strongly in the NIR region of the spectrum and holds great promise as a bridging ligand for strong exchange coupled polynuclear metal

clusters. The synthetic methodology to **3** can also be adapted to larger polytopic ligands that we are currently synthesizing and will report on shortly.

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#### Notes and references

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\*Electronic Supplementary Information (ESI) available: Synthetic details, crystal data & cif, EPR, electrochemical and computational information for **2** and **3**. See DOI: 10.1039/c000000x/

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