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Polynuclear Cu_4L_4 Copper(II) Aminyl Radical Coordination Complexes

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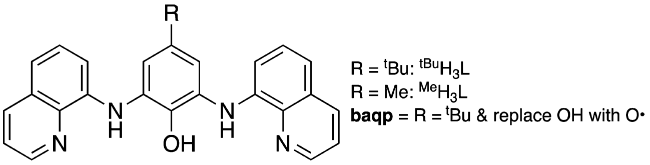
Supporting Information

ABSTRACT: We describe the structural features and magnetic properties of two polynuclear copper(II) complexes containing a redox-active ligand. These neutral complexes each bear the formula RL_4Cu_4 (R = ^{t}Bu, Me) with the ligand in a dianion-aminyl radical oxidation state. X-ray data and density functional theory calculations support an aminyl-type radical character in these complexes, making these the first polynuclear metal aminyl radical complexes.

The coordination chemistry of free-radical ligands is a well-developed branch of inorganic chemistry.[1−9] Strong direct magnetic exchange coupling between paramagnetic transition-metal ions with open-shell ligands is an avenue toward bulk magnetic materials comprised of molecular precursors rather than traditional atom-based materials.[1] Spectacular examples of *molecule-based magnets* using this "metal-radical" approach have been reported using different free-radical types.[2,10,11] Strong magnetic exchange coupling in metal-free radical complexes has also been exploited to produce *single-molecule-magnet* behavior.[5] Some of these reports have shown that strong exchange coupling in tandem with large magnetoanisotropy can result in large magnetization relaxation barriers and open thermal hysteresis loops up to reasonably high temperatures.[12−18]

Recently, we reported the synthesis and properties of an unusually stable phenoxyl radical, 2,6-bis(8-quinolylamino)-4-*tert*-butylphenoxyl (baqp; Chart 1).[19] The baqp radical is produced from air or chemical oxidation of the phenol precursor ($^{t\mathrm{Bu}}H_3L$; Chart 1) and has a ditopic structure that looks amenable to building polynuclear coordination complexes with the advantage of a bridging O atom that is spin-density-rich. Herein, we describe the synthesis of the 4-methyl-substituted analogue to $^{t\mathrm{Bu}}H_3L$ ($^{\mathrm{Me}}H_3L$; Chart 1) and the first coordination complexes with both ligands. To our surprise, coordination of $^{t\mathrm{Bu}}H_3L$ and $^{\mathrm{Me}}H_3L$ to $Cu(ClO_4)_2\cdot 6H_2O$ resulted in the formation of RL_4Cu_4 [R = ^{t}Bu (**1**), Me (**2**)] clusters, where the ligand can only be described as an *aminyl* radical, not a phenoxyl radical. The X-ray crystal structures and magnetic properties of **1** and **2** are described, and these experimental results are supported by density functional theory (DFT) calculations. There are very few reported examples of metal aminyl radical complexes[20−30] and, to our knowledge, none that are polynuclear.

Chart 1. Structures of Ligands Used in This Work



Ligand $^{t\mathrm{Bu}}H_3L$ was prepared as described previously,[19] and $^{\mathrm{Me}}H_3L$ was prepared similarly (Scheme S1 and Figures S4 and S5). Complexes **1** and **2** were prepared by reacting equimolar amounts of the ligands with $Cu(ClO_4)_2$ in methanol in the absence of air (the synthetic details for all new compounds are given in the Supporting Information). Maroon precipitates were immediately formed, and single crystals suitable for X-ray diffraction were grown from tetrahydrofuran/toluene solutions of the precipitates. The spectroscopic properties of the methanol precipitates are nearly identical with those of the single crystals (Figures S8 and S9). Powder X-ray diffraction (pXRD) patterns of the powders match well to the calculated pXRD patterns (Figures S10−S13). The electrospray ionization mass spectrometry (ESI-MS) spectrum of complex **1** exhibited a peak at *m*/*z* that corresponds to $[M + H]^+$ with the correct isotope distribution for the $^{t\mathrm{Bu}}L_4Cu_4$ formulation (Figure S6). Complex **2** is less stable than **1**, and we identified a peak at *m*/*z* corresponding to $[M + 4H]^+$ in the ESI-MS spectrum of **2** (in protic solvents, it is likely that these complexes decompose by H-atom abstraction reactions). There is no perchlorate evident in the ESI-MS spectrum of **1** or **2** or in the Fourier transform infrared (FT-IR) spectrum of the complexes.

The molecular structures of **1** and **2** are shown in Figures 1 and S1, respectively (Tables S1−S4). An alternative view of the molecular structure of **1** is shown in Figure 2 (Figure S2 for **2**), and the Cu_4O_4 core structure is illustrated in Figure 2 (Figure S3 for **2**).

1 and **2** are neutral complexes of the form $^{t\mathrm{Bu}}L_4Cu_4$ or $^{\mathrm{Me}}L_4Cu_4$. No perchlorate was found in the lattice, but solvent molecules are present. The regular M_4L_4 "square" or [2 × 2] grid structures[31−35] that we initially anticipated were not formed as a result of an unusual ligand conformation. Each Cu ion is five-coordinate with a distorted square-pyramidal coordination geometry (Figure 2, right). The Cu ion is coordinated to three donors (O, N_{amido}, and N_{quin}) from the same ligand as well as O and N_{aminyl} donors from a different ligand. The three donors from one ligand and the O donor from the other ligand comprise the basal plane. These coordinate bonds are short and suggest a divalent oxidation state assignment for the Cu ion. An alternative

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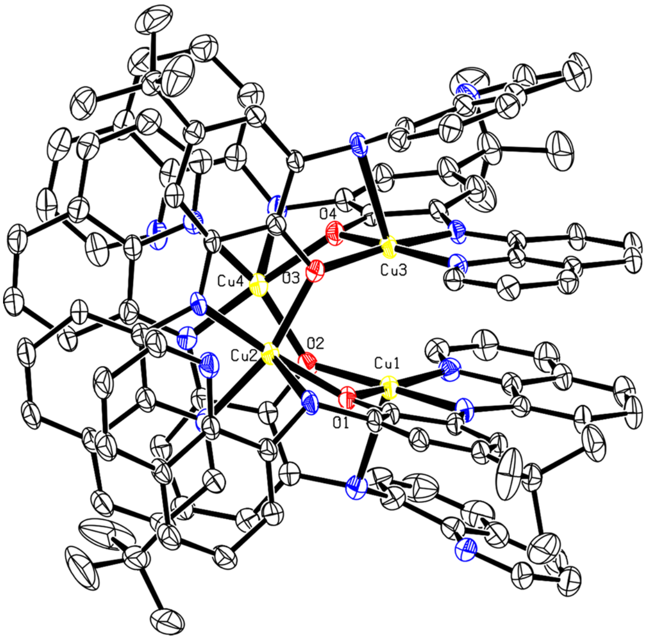

Figure 1. Molecular structure of **1** (displacement ellipsoids at 30% probability). H atoms and solvent molecules removed for clarity.

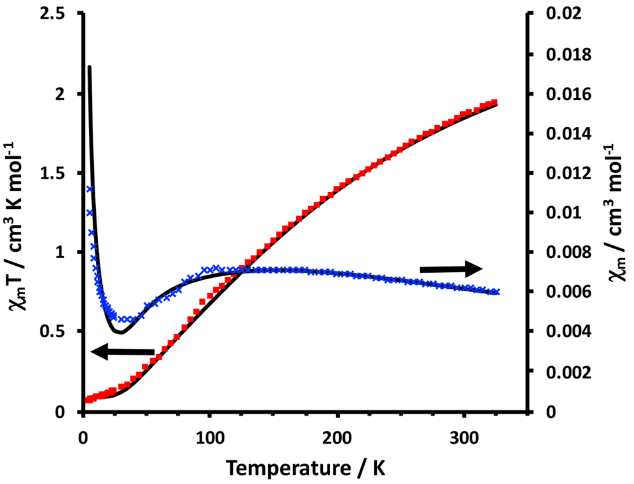

Figure 3. Variable-temperature magnetic susceptibility data for **1** at an external field of 5000 Oe. Red squares and blue crosses are the data points, and the black line represents the best fit to the experimental data using the model described in the text.

oxidation state of 3+ for Cu with the ligand binding as a closed-shell trianion with two amido and one phenolate donors would generate a diamagnetic complex, which is not observed experimentally. The coordinate bond distances in the basal plane range from 1.905(4) to 1.973(3) Å for Cu(1) and are very similar for all four Cu ions. The other N_{aminyl} donor provides the axial coordinate bond, which is very long; the average axial coordinate bond length is 2.588 Å. These binding features produce an irregular bridging Cu_4O_4 core structure (Figure 3) with a Cu−O−Cu bond angle that ranges from 120.34(18) to 127.12(18)°.

The Cu^{2+} oxidation state assignment in **1** requires that the coordinated ligand is a dianion to satisfy charge balance. One possibility is that the coordinated ligand is not fully deprotonated; however, in the FT-IR spectra of **1** and **2**, there is no evidence of an O−H or N−H stretch, and no H atoms could be located on the N or O atoms in the X-ray structure. Inspection of the coordinated ligand in the structure of **1** and **2** reveals an irregular conformation: One quinoline ring is coplanar with the central ring, and the N, N, and O donor atoms from this portion of the ligand form the basal coordination plane of the Cu ions. The plane containing the other quinoline ring is nearly perpendicular to the plane containing the rest of the ligand atoms, and this quinoline ring is therefore unconjugated from the rest of the ligand. The C−N bond joining this rotated quinoline ring to the ligand is long [ranging from 1.438(7) to 1.461(6) Å], significantly longer than the other C−N bond joining the coplanar quinoline ring to the central ring [1.375(6)−1.392(7) Å]. The central ring C−C bond distances reveal a regular aromatic ring structure [C−C bond distances for the four rings are similar and range from 1.376(7) to 1.430(6) Å in one of the four rings], and the long C−O bond distances [range from 1.354(6) to 1.381(6) Å] are indicative of a bound phenolate. In uncoordinated baqp, the structural features of the central ring and the short C−O distance [1.255(2) Å] are typical for a phenoxyl radical.[19] In a handful of structurally characterized metal phenoxyl radical complexes, the C−O bond distance is typically much shorter, generally under 1.3 Å in length.[36−38] These observations indicate that the ligand dianion radical in complexes **1** and **2** is not a phenoxyl radical. Our structural data and DFT calculations point to a structure with N_{amido} and O anionic donor atoms from the coplanar part of the ligand, and the other rotated quinoline ring is joined to the ligand via a localized aminyl radical (Figure 2).

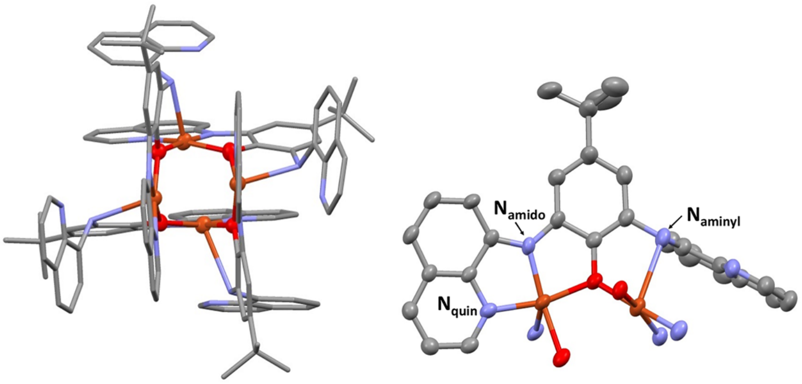

Figure 2. Left: View of the molecular structure of **1** highlighting the Cu_4O_4 core and the long axial Cu−N coordinate bonds. Right: Closeup of one of the Cu_2L units.

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The UV−visible−near-IR (NIR) spectra of complexes **1** (Figure S14) and **2** exhibit a strong visible absorption band (523 and 517 nm for **1** and **2**, respectively). Upon exposure to air or after oxidation with $AgPF_6$, new intense and broad absorptions appear across the visible and NIR spectrum. These transitions are assigned as intervalence charge-transfer bands. The oxidation of **1** or **2** is ligand-centered and produces ligand mixed-valent states. Complexes **1** and **2** are stable under inert conditions in the solid state and in solution but will decompose over a period of several hours in the solid state in air and nearly instantly upon exposure to air in solution.

The variable-temperature magnetic susceptibility properties of **1** and **2** were recorded at a field of 5000 Oe over a temperature range of 5−325 K (Figures 3 and S16). The data profiles are very similar to each other, and the broad maxima in the χ_m versus T profile suggest strong intramolecular antiferromagnetic coupling. The values of $\chi_M T$ for **1** and **2** at 325 K are 1.88 and 1.90 $cm^3\ mol^{-1}$ K, respectively. This is less than the theoretical value (3.00 $cm^3\ mol^{-1}$ K) for four uncoupled Cu^{II} ions and $S = {}^1/_2$ radicals with $g = 2$, pointing to strong antiferromagnetic coupling within the cluster. With decreasing temperature, there is a steady decrease in $\chi_M T$ tending toward a value of zero at 5 K, revealing an $S = 0$ ground state for complexes **1** and **2**. Using the *PHI* program,[39] we obtained very good fits to the experimental data using a spin Hamiltonian (Figure S15), incorporating one exchange coupling constant in our model (J = Cu-radical). On the basis of the similarities in the coordination environment of each Cu ion and the coordinated ligand structures, we assumed that the Cu-radical exchange coupling constants would be approximately the same. For complex **1**, we obtained the following best-fit parameters: $J_{\text{Cu-rad}} = -92\ cm^{-1}$, $g_{av} = 2.050$, $zJ' = -0.91\ cm^{-1}$, temperature-independent paramagnetism (TIP) = $1.19 \times 10^{-4}\ cm^3\ mol^{-1}$, $\rho = 0.029$, and residual = 0.013. Another model that incorporated two different exchange coupling constants, including also a Cu−Cu exchange coupling in addition to the Cu-radical exchange, resulted in good fits, but with unrealistically large antiferromagnetic couplings in excess of $-250\ cm^{-1}$ in both cases. The best-fit parameters for complex **2** are very similar to those found for **1** (Figure S16). The antiferromagnetic coupling between the ligand radical and Cu^{II} ion is a direct exchange interaction. Given the very long coordinate bond between spin-density-rich N_{aminyl} and Cu, the exchange is likely mediated by bridging O atoms, which bear a smaller but significant spin density in the complexes.[40,41]

Using the coordinates from the X-ray structures, we carried out single-point-energy calculations on complexes **1** and **2** in a restricted singlet state (B3LYP/def2-svp). The converged wave functions were not stable and were reoptimized to unrestricted wave functions. The Mulliken spin densities were calculated for complexes **1** and **2** (Figures S17 and S18 and Table S5 and S6). Large alternating α and β spin densities are found on the Cu ions around the Cu_4O_4 core (±0.60); large spin densities are also found on the axially coordinated N_{aminyl} atoms that are bonded to the rotated quinoline rings (Mulliken spin densities on N_{aminyl} atoms are +0.63, −0.66, +0.62, and +0.66 and that on an O atom is ±0.05). To our knowledge, complexes **1** and **2** are the first examples of polynuclear clusters containing multiple aminyl radical ligands.

The complexes described in this work have expanded the scope of metal aminyl chemistry. The “ambi-radical” character of these ligands, changing from a neutral phenoxyl radical when uncoordinated to a dianion-aminyl radical when fully deprotonated and coordinated, is another unusual aspect of this work that we are pursuing with the synthesis of other ligand derivatives. The strong exchange coupling in **1** and **2** augurs well for the production of high-spin ground-state complexes with other metal ions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00785.

> Synthetic details, spectroscopic, X-ray, and variable-temperature magnetic data for **2**, and computational data (PDF)

Accession Codes

CCDC 1832268−1832269 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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