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Effect of Ligand Substituent Coordination on the Geometry and the Electronic Structure of Cu(II)-Diradical Complexes[§]

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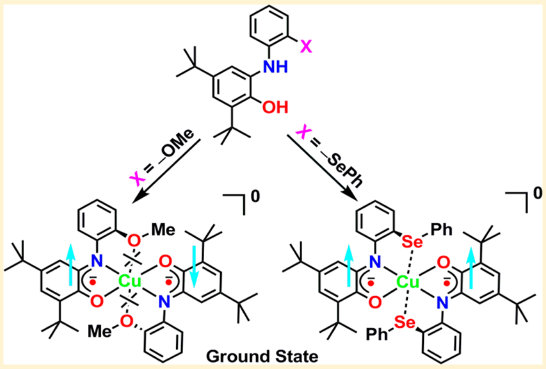
Supporting Information

ABSTRACT: Two organic moieties, known as ligands, having −OMe and −SePh as the ortho substituent attached to the aniline moiety of the parent 2-anilino-4,6-di-*tert*-butylphenol ligand, were synthesized. The ligands reacted with $CuCl_2{\cdot}2H_2O$ in a 2:1 ratio in CH_3CN in the presence of Et_3N and provided the corresponding mononuclear Cu(II)-diradical complexes **1** (−OMe) and **2** (−SePh). Complex **1** was square planar, while complex **2** was in distorted square planar geometry due to the secondary coordination between the Se atom and the central Cu(II) center. Both complexes were comprised of multi-paramagnetic centers and exhibited an $S_t = 1/2$ ground state as established by variable-temperature magnetic susceptibility measurements. X-band electron paramagnetic resonance measurements indicated the presence of an unpaired electron at the Cu(II) center in complex **1** and at the ligand center (*π*-radical) in complex **2**. The extent of the secondary interaction was found to be dependent on the "softness" of the donor atom belonging to the ortho substituent.

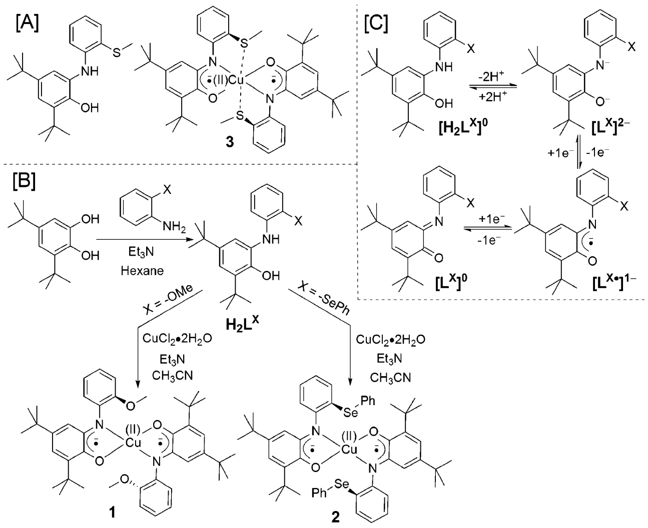


INTRODUCTION

Mononuclear Cu(II) ion containing metalloenzyme galastose oxidase (GOase) selectively catalyzes aerial oxidation of primary alcohols to their corresponding aldehydes, with concomitant reduction of molecular oxygen to H_2O_2.[1] Because of the structural simplicity and high utility as oxidation catalyst, synthesis of radical(s)-containing Cu(II) complexes as structural and/or functional models of GOase has drawn considerable attention.[2] In this regard, several Cu(II)-diradical complexes were synthesized.[2a,g,i−k] In those complexes the ground state is predominated by a Cu(II)-centered unpaired electron, which was caused by the stronger antiferromagnetic coupling between the two radical centers than that between the Cu(II) and a radical center. Although incorporation of different functional groups or steric crowding at the ligand backbone changes the dihedral angle (i.e., the angle between two ligating O−Cu−N planes, and will be noted here as distortion) around the Cu(II) center up to 35.5°,[2i,j] no alteration in the coupling fashion between the radicals and the Cu(II) and a radical centers are known.

In contrast to the conventional coupling fashion, in 2005 Kaim and coworkers[2k] showed that the presence of a −SMe substituent at the ligand backbone (at the ortho position of the aniline moiety, Scheme 1) in a Cu(II)-diradical complex (**3**) can alter the coupling fashion; that is, antiferromagnetic coupling between the two radicals is less than that of the Cu(II) and a radical. It is proposed that the change in the coupling fashion is due to the 32.2° dihedral angle between two ligating O−Cu−N planes, caused by the weak secondary

Scheme 1. Schematic Representations of (a) the Ligand and the Corresponding Cu(II) Complex Reported by Kaim and Coworkers, (b) Synthetic Route for H_2L^{OMe} and H_2L^{SePh} and Their Corresponding Cu(II)-Diradical Complexes, and (c) the Possible Different Redox-States of the Ligands



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interaction between the Cu(II) center and the S atom from the −SMe substituent. However, it is known that Cu(II)-diradical complex having 35.5° dihedral angle around the Cu(II) center with no secondary interaction does not alter the coupling fashion.[2j] This acute observation indicates that the alteration in the coupling fashion might not be solely because of the distortion around the Cu(II) center but is rather possibly due to the secondary interaction that promotes a geometrical change in the complex. Because of this change the couplings fashion, and the coupling magnitude between the paramagnetic centers might change over. To find out the actual fact, we have employed two ligands by placing −OMe and −SePh at the ortho position of the aniline moiety (Scheme 1). We chose −OMe and −SePh substituted ligand because both of them could interact with the Cu(II) center. Additionally, on going from O to Se the "hardness" of the donor atom will decrease and consequently the Cu−substituent interaction (secondary coordination) should increase. Hence, the extent of interaction and its effect on the geometry as well as electronic structure of the corresponding Cu(II)-diradical complexes can be evaluated. Herein, we report the synthesis and characterization of ligand H_2L^{OMe}, H_2L^{SePh}, and their corresponding Cu(II)-diradical complexes (Scheme 1). The effect of secondary coordination on the geometry and the electronic structure of the Cu(II) complexes are presented.

■ RESULTS AND DISCUSSION

Ligands H_2L^X (X = −OMe and −SePh) were synthesized by reacting equimolar amounts of 3,5-di-*tert*-butylcatechol and the corresponding amine in the presence of Et_3N in hexane (Scheme 1). Reaction of the individual ligand (H_2L^{OMe} or H_2L^{SePh}) with $CuCl_2{\cdot}2H_2O$ in a 2:1 ratio in CH_3CN in the presence of Et_3N provided the corresponding Cu(II)-diradical complexes **1** and **2**, respectively (Scheme 1). Single crystals for **1** $[\{Cu^{II}(L^{OMe\cdot})_2\}{\cdot}H_2O]$ and **2** $[\{Cu^{II}(L^{SePh\cdot})_2\}]$ were obtained by recrystallizing the corresponding complex from a 5:2 CH_2Cl_2/CH_3CN solvent mixture. The molecular structures are presented in Figure 1. Selected bond distances and bond angles are given in Table 1.

In both neutral complexes (**1** and **2**) the central copper atom was coordinated by two ligand-centered N as well as O atoms. Although the Cu(1)−N(1) = 1.935(3) [**1**], 1.940(3) Å [**2**] (brackets indicate the complex) bond distance was almost same for both complexes and was in accord with the +II oxidation state of the copper center,[2i−l] a remarkable elongation (0.055 Å) in Cu−O bond distance {Cu(1)−O(1) = 1.908(3) [**1**], 1.963(2) Å [**2**]} due to secondary coordination, Cu(1)−Se(1) = 3.076(1) Å, was observed in **2**. Furthermore, the secondary coordination caused a large deviation in the O1−Cu(1)−O(1i) bond angle {180.00(11) [**1**], 143.79(5)° [**2**]}. The geometry around the copper center in **1** was square planar ($\tau = 0.0°$) with no Cu−O_{Me} (O_{Me} indicates O atom from the −OMe group), 3.513(4) Å, interaction from the two oppositely (trans) oriented −OMe groups attached at the ortho position of the aniline moiety (Figure 1). On the contrary, a distorted square planar geometry ($\tau = 26.2°$), which can also be considered as pseudo-octahedron, with a large dihedral angle (36.6°) between the two N(1)−Cu(1)−O(1) planes was observed in **2**. Interestingly, in complex **2**, two −SePh groups were situated cis to each other.

The C−C bond distances of the *tert*-butyl-containing C_6 rings in both **1** and **2** were not equal and were falling within the 1.39 ± 0.01 Å range. This indicated that the rings were not actual phenyl rings. An alternating short and long C−C bond distance showed a quinoid-type distortion. This type of distortion was expected for phenyl ring with its oxidized form(s) (Scheme 1). Additionally, the C(1)−N(1) = 1.341(4) [**1**], 1.349(2) Å [**2**] and C(2)−O(1) = 1.294(4) [**1**], 1.293(3) Å [**2**] bond distances, which were between their single bond and double bond character, confirmed one-electron oxidized iminobenzosemiquinone form $\{[L^{X\cdot}]^-$, Scheme 1} of the coordinating ligands in **1** and **2**.[2i−l] Therefore, from the X-ray single-crystal analysis, both complexes can be described as Cu(II)-diradical.

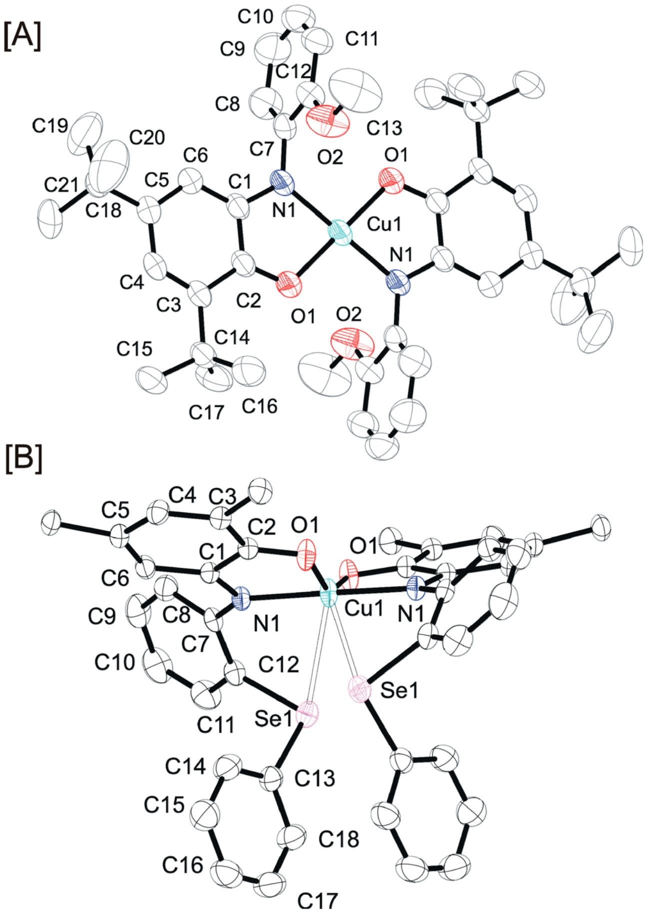

Figure 1. Molecular structure of (a) complex **1** and (b) complex **2**; thermal ellipsoids were drawn at 50% probability. Hydrogen atoms, solvent molecules, and methyl group attached to the *tert*-butyl groups (only in **2**) were omitted for clarity.

Variable-temperature magnetic susceptibility measurements for both **1** and **2** are shown in Figure 2 as a plot of μ_{eff} versus T. Both complexes were composed of three paramagnetic centers with one unpaired electron on each (vide supra). At 10 K, μ_{eff} = 1.82 μ_B (**1**) and μ_{eff} = 1.73 μ_B (**2**) were observed (parentheses indicates the complex). These values were in accord with an S = 1/2 ground state for both complexes and discarded the possible ferromagnetic coupling among the three paramagnetic centers. A higher μ_{eff} value (>1.73 μ_B) in **1** was related to the higher g value (g > 2.00) and indicated that the unpaired electron was residing on Cu(II) center. The μ_{eff} = 1.73 μ_B value in **2** arose due to the presence of radical-centered unpaired electron (g = 2.00). In **1**, the μ_{eff} value remained almost constant up to 150 K, then increased slightly and gradually with the increase in temperature, and reached at 2.06 μ_B at 300 K. This feature

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 1 and 2

	1	2
Cu1−N1	1.935(3)	1.940(3)
Cu1−O1	1.908(3)	1.963(2)
C1−N1	1.341(4)	1.349(2)
N1−C7	1.421(4)	1.411(3)
C2−O1	1.294(4)	1.293(3)
C1−C2	1.449(4)	1.453(3)
C2−C3	1.424(4)	1.439(3)
C3−C4	1.363(4)	1.374(3)
C4−C5	1.418(4)	1.430(3)
C5−C6	1.371(4)	1.366(3)
C6−C1	1.409(4)	1.421(3)
C7−C8	1.381(6)	1.404(3)
C8−C9	1.375(6)	1.385(3)
C9−C10	1.372(7)	1.381(4)
C10−C11	1.341(6)	1.368(3)
C11−C12	1.390(5)	1.386(3)
C12−C7		1.405(3)
C13−C14		1.383(3)
C14−C15		1.383(4)
C15−C16		1.388(4)
C16−C17		1.356(4)
C17−C18		1.391(4)
C18−C13		1.381(3)
O2−C12	1.346(5)	
O2−C13	1.436(6)	
Se1−C12		1.922(2)
Se1−C13		1.923(2)
N1−Cu1−N1i	180.00(11)	179.30(6)
O1−Cu1−O1i	180.00(11)	143.79(5)
N1−Cu1−O1	83.84(11)	83.29(6)
N1−Cu1−O1i	96.16(11)	96.93(6)
Cu1−N1−C1	112.6(2)	113.10(12)
Cu1−O1−C2	113.20(21)	112.24(12)
N1−C1−C2	113.20(28)	113.54(16)
O1−C2−C1	117.09(26)	117.68(16)
C12−O2−C13	117.28(31)	
C12−Se1−C13		99.78(9)

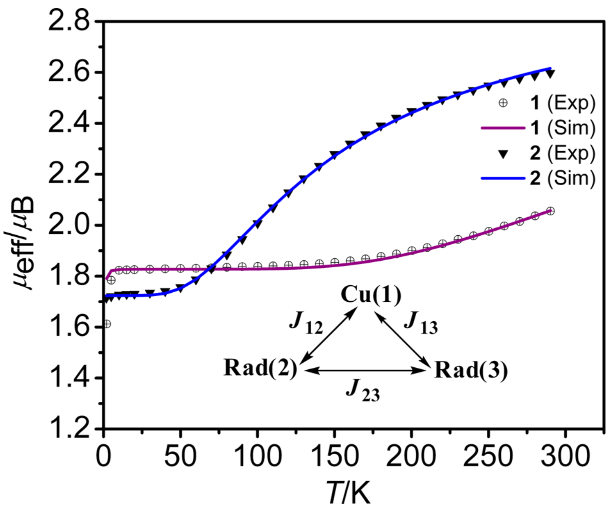

Figure 2. Showing μ_{eff} vs T plots for **1** and **2**.

consolidated the presence of multi-paramagnetic centers, and indicated the energy difference between the ground state (S = 1/2) and the higher spin state (S = 3/2) as high (>105 cm^{-1}, as 1 K ≈ 0.7 cm^{-1}). In the case of **2**, the μ_{eff} value started increasing gradually at 45 K and reached almost to a plateau at 300 K (μ_{eff} = 2.62 μ_B). This feature showed the existence of energetically low-lying S = 3/2 spin state (~32 cm^{-1}, as 1 K ≈ 0.7 cm^{-1}). The experimental results were simulated (Figure 2) using the following parameters: [**1**], $g_{\mathrm{Cu(II)}}$ = 2.10, g_R = 2.00, J_{12} = J_{13} = 0.0 cm^{-1}, J_{23} = −342.0 cm^{-1}, and [**2**], $g_{\mathrm{Cu(II)}}$ = 2.03, g_R = 2.00, J_{12} = J_{13} = −64.0 cm^{-1}, J_{23} = −23.0 cm^{-1}.[3]

The interactions between the three unpaired electrons will provide electronic spin states (S_t, S^*) = (3/2, 1), (1/2, 1), and (1/2, 0), where S_t = S_{Cu} + S_{rad1} + S_{rad2} and S^* = S_{rad1} + S_{rad2}. These electronic spin states can be symbolically represented as (↑↑↑), (↑↓↑), and (↑↑↓), respectively. The observed S = 1/2 ground state for both complexes indicated that the electronic spin state (3/2, 1) was higher in energy compared to the others. The S = 1/2 ground state could appear due to the presence of an unpaired electron either on a Cu(II) center or on a radical center. The ground state electronic configuration (↑↑↓) would provide Cu(II)-centered electron paramagnetic resonance (EPR) spectrum, while (↑↓↑) would provide a radical-centered EPR spectrum. Therefore, to define the exact location of unpaired electron and ground state electronic configuration, X-band EPR measurements were performed for both complexes at 77 K in a 1:1 CH_2Cl_2/toluene solvent mixture and depicted in Figure 3.

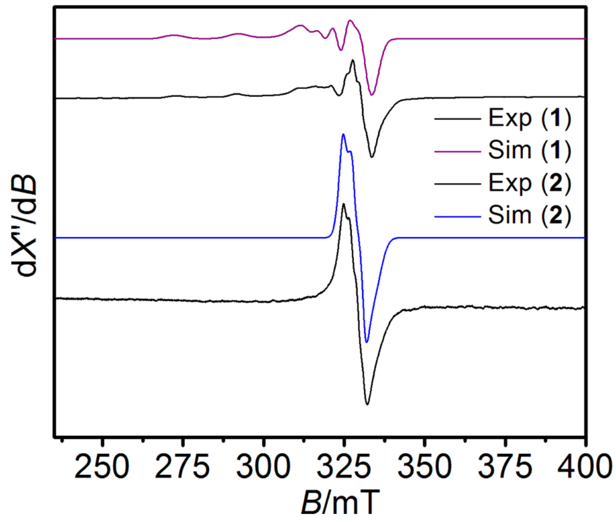

Figure 3. Experimental (Exp) X-band EPR spectrum for **1** and **2** presented with simulation (Sim). X-band microwave frequency (GHz): 9.125 [**1**], 9.145 [**2**]; modulation frequency (kHz): 100 [**1**, **2**].

Simulation of the experimental results provided the following parameters: [**1**], (g_1, g_2, g_3) = 2.000, 2.025, 2.170, g_{av} = 2.065; Cu(A_1, A_2, A_3) = (33, 43, 173) × 10^{-4} cm^{-1}, N(A_1, A_2, A_3) = (6, 7, 2) × 10^{-4} cm^{-1}, and [**2**], (g_1, g_2, g_3) = 1.964, 1.992, 1.992, g_{av} = 1.983; (A_1, A_2, A_3) = (13, 30, 30) × 10^{-4} cm^{-1}, Cu(A_1, A_2, A_3) = (10, 10, 8) × 10^{-4} cm^{-1}. Complex **1** exhibited a slight rhombic signal with $g_{\parallel} > g_{\perp}$ and g_{av} = 2.065. This type of signal is common for square planar Cu(II) complexes with $(d_{x^2-y^2})^1$ magnetic orbital.[2i,j,l] Hence, the (↑↑↓) ground state prevailed in **1** with dominating antiferromagnetic coupling between the radicals. Unlike complex **1**, an axial signal at g_{av} = 1.983 was observed in complex **2**. This indicated a radical-centered unpaired electron and (↑↓↑) as the ground-state electronic configuration owning stronger antiferromagnetic coupling between the Cu(II) and a radical center.[2k] These results agreed well with the variable-temperature magnetic susceptibility measurements. The lower g_{av} value [<2.0023 (free radical)] in **2** emphasized the fact that spin state with nonzero orbital angular momentum situated at low energy.[4] Herein, it is important to note that g_{av} = 1.983 in **2** was much lower than that of g_{av} = 2.0006 observed for the Cu(II)-diradical complex with −SMe as the ortho substituent (**3**). This higher g_{av} deviation from 2.0023 in **2** than in **3** implicated a greater extent of interaction, due to low energy difference, between the ground state and the excited state with nonzero orbital angular momentum. This was possible due to the higher "softness" of the donor Se atom compared to the donor S atom.

■ CONCLUSIONS

To conclude, two Cu(II)-diradical complexes were synthesized by placing −OMe and −SePh as the ortho substituents. Hard donor O atom did not undergo secondary coordination with the Cu(II) center, while soft donor Se atom did. Because there was no secondary coordination, complex **1** was square planar. A distorted square planar or a pseudo-octahedral geometry was found in **2** because of the secondary coordination. It was observed that the higher softness of the donor atom caused (i) higher secondary coordination [Cu−S = 3.336(av), Cu−Se = 3.076 Å], (ii) more distortion [τ(**1**, **3**, **2**) = (0, 32.2,[2k] 36.6)°], and (iii) elongation in the Cu−O bond distance with higher deviation in the O−Cu−O bond angle [{**1**} = 1.908, 180.0; {**3**} = 1.923 (av), 149.7; {**2**} = 1.963 Å, 143.8°]. Interestingly, no significant deviation was caused by the secondary coordination in the N−Cu−N bond angle [{**1**} = 180.0; {**3**} = 172.0; {**2**} = 179.3°].

In the square planar complex **1** (τ = 0.0°), the radical-centered magnetic orbitals (p_z orbitals) were orthogonal to the Cu(II) $\{d_{x^2-y^2}\}$ orbital. The two radicals were coupling to each other through the Cu(II)-centered t_{2g} orbital. This coupling is strongly antiferromagnetic in nature[2f] and dominated over the Cu(II) and a radical center coupling magnitude and provided (↑↑↓) as the ground state. On the contrary, because of the secondary interaction a remarkable deviation from the linearity in the O−Cu−O bond angle occurred in **2** (Table 1). Because of this deviation, the orthgonality between the radical-centered and the Cu(II)-centered magnetic orbitals was lost. Thus, an antiferromagnetic coupling between the magnetic orbitals appeared. Furthermore, the extent of antiferromagnetic interaction between the two radical centers was diminished due to the deviation in the O−Cu−O bond angle. In complex **2** (∠ O−Cu−Oi = 149.7°), the ligand-centered radicals interacted strongly with the Cu(II)-centered magnetic orbital and underwent a higher extent of coupling (antiferromagnetic) than did the two radicals. This caused (↑↓↑) to be the ground state. Herein, it is important to note that the previously reported Cu(II)-diradical complex[2j] having (i) 35.5° dihedral angle, (ii) no secondary interaction, and (iii) (↑↑↓) as the ground state shows two cross angles (cross angle = the two largest angles around the central metal atom in a square planar complex) as 155.1 and 157.4°. These indicate an almost same deviation from the linearity in both cross angles, while we observed almost linearity in one of the two cross angles (Table 1); the other was <150°, to have (↑↓↑) as the ground state. Hence, it is evident now that the dihedral angle is not the factor that alters the couplings fashion. It is mainly the secondary coordination that causes a geometrical change in terms of the deviation only in one of the two cross angles, and consequently promotes an alteration in the couplings fashion and their magnitudes between magnetic orbitals.

■ EXPERIMENTAL SECTION

General Considerations. All the chemicals and solvents were obtained from commercial sources and were used as supplied, unless noted otherwise. The 3,5-di-*tert*-butylcatechol, *o*-anisidine, diphenyl diselenide, and 2-fluoronitrobenzene were purchased from Sigma-Aldrich. Solvents were obtained from Merck (India). Air-sensitive reaction was performed under Ar atmosphere using proper glass apparatus.

Physical Methods. X-ray crystallographic data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo Kα radiation (λ = 0.71073 Å) at 296(2) K, with increasing *w* (width of 0.3° per frame) at a scan speed of 3 s/frame. Structures were solved by direct methods using SHELXS-97 and refined with full-matrix least-squares on F^2 using SHELXL-97.[5] All the non-hydrogen atoms were refined anisotropically.

IR spectra were recorded on Perkin-Elmer instrument at normal temperature with KBr pellet by grinding the sample with KBr (IR grade). UV−visible spectra were recorded on Perkin-Elmer, Lamda 750, UV−vis−near-IR spectrometer by preparing a known concentration of the samples in high-performance liquid chromatography (HPLC) grade CH_2Cl_2 at room temperature using a cuvette of 1 cm width. EPR spectra were measured on X-Band Microwave unit, JES-FA200 ESR spectrometer. Mass spectral (MS) data were obtained from quadrupole time-of-flight (QTOF)-MS spectrometer. Variable-temperature magnetic susceptibility measurements were performed using superconducting quantum interference device (SQUID) magnetometer at 1 T (**1**) and 0.1 T (**2**).

Synthesis of [$C_{21}H_{29}NO_2$], H_2L^{OMe}. Synthesis of this ligand was reported previously.[6]

Synthesis of [$C_{26}H_{31}NOSe$], H_2L^{SePh}. To a solution of 3,5-di-*tert*-butylcatechol (2.54 g, 11.47 mmol) and 2-(phenylselanyl)aniline (2.85 g, 11.47 mmol) in hexane (25 mL), Et_3N (0.05 mL) was added. The resulting solution was stirred for 48 h at room temperature (30 °C). A dark brown solution was obtained with an orange precipitate. The mixture was filtered and washed with hexane (10 mL). The brown filtrate was evaporated in vacuo to give a viscous brown liquid as crude product. The crude product was purified by column chromatography on silica gel (60−120 mesh) with ethyl acetate−hexane (1:9) as the eluent. The product was afforded as yellow viscous liquid. Yield: 2.78 g, 54%. Fourier transform infrared (FTIR) (KBr pellet cm^{-1}): 3433, 3322, 2956, 2905, 2867, 1583, 1476, 1362, 1309, 1021, 734, 689. ^{1}H NMR ($CDCl_3$, 399.85 MHz): δ 1.21 (s, 9H), 1.39 (s, 9H), 6.04 (s, 1H), 6.06 (s, 1H), 6.48 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.77 (d, *J* = 2 Hz, 1H), 6.81 (dt, *J* = 7.2, 1.2 Hz, 1H), 7.19−7.30 (m, 7H), 7.71 (dd, *J* = 7.6, 1.6 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 29.5, 31.6, 34.4, 35.0, 109.8, 114.0, 114.7, 119.8, 122.1, 122.5, 126.7, 127.1, 129.3, 129.5, 129.6, 131.3, 131.1, 135.3, 138.4, 142.3, 148.5, 149.7 ppm. ESI-MS (+) *m/z* for [$C_{26}H_{31}NOSe$ + H]$^+$: Calcd, 454.1703; found, 454.1679. Anal. Calcd for $C_{26}H_{31}NOSe$: C, 68.85; H, 6.89; N, 3.10. Found: C, 68.66; H, 7.09; N, 3.20%.

*Synthesis of [$C_{42}H_{54}CuN_2O_4 \cdot H_2O$], **1**.* To a stirred solution of H_2L^{OMe} (0.328 g, 1.00 mmol) in CH_3CN (20 mL), $CuCl_2 \cdot 2H_2O$ (0.090 g, 0.53 mmol) and Et_3N (0.2 mL) were added sequentially. The reaction mixture was stirred for 2.5 h at room temperature. This caused a brown-black precipitation. The precipitate was filtered and washed with CH_3CN. Recrystallization of the solid from a CH_2Cl_2/CH_3CN (5:2) solvent mixture provided a crystalline compound suitable for single-crystal X-ray diffraction study. Yield: 0.204 g, 56%. FTIR (KBr pellet, cm^{-1}): 3434, 3071, 2956, 2906, 2867, 2853, 1580, 1508, 1490, 1463, 1435, 1422, 1387, 1360, 1333, 1301, 1256, 1244, 1204, 1174, 1113, 1043, 1025, 996, 926, 911, 881, 787, 775, 746, 693, 644, 604, 500. ESI-MS (+) *m/z* for [$C_{42}H_{54}CuN_2O_4$]$^+$: Calcd, 713.35; found, 713.37. UV−vis−NIR (CH_2Cl_2) λ_{max}, nm (ε, M^{-1} cm^{-1}): 1030(2600), 780(6750), 472(5600), 340(17 200), 305(20 050). Anal.

Calcd for $C_{42}H_{54}CuN_2O_4{\cdot}0.7H_2O$: C, 69.43; H, 7.69; N, 3.86. Found: C, 69.84; H, 7.47; N, 3.89%.

Synthesis of [$C_{52}H_{58}CuN_2O_2Se_2$], ***2.*** To a solution of H_2L^{SePh} (0.305 g, 0.67 mmol) in CH_3CN (10 mL), $CuCl_2{\cdot}2H_2O$ (0.062 g, 0.35 mmol) was added followed by addition of Et_3N (0.1 mL). The reaction solution was then stirred for 16 h. This caused precipitation of a black solid. The solid was washed with CH_3CN and then dried under air. The solid was then recrystallized from a 5:1 CH_2Cl_2/CH_3CN solvent mixture. A brown-black crystalline solid suitable for single-crystal X-ray study appeared in 2 d. Yield: 0.200 g, 55%. FTIR (KBr pellet, cm^{-1}): 3429, 2949, 2904, 2866, 1462, 1424, 1250, 1022, 739, 687. ESI-MS (+) m/z for $[C_{52}H_{58}CuN_2O_2Se_2]^+$: Calcd, 965.23; found, 965.23. UV−vis−NIR (CH_2Cl_2) λ_{max}, nm (ε, M^{-1} cm^{-1}): 1036(2900), 806(6050), 460(5850), 342(18 250), 294(23 650). Anal. Calcd for $C_{52}H_{58}CuN_2O_2Se_2$: C, 64.65; H, 6.06; N, 2.90. Found: C, 64.28; H, 6.14; N, 2.73%.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of crystallographic structural parameters for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 935848 (**1**·$1H_2O$) and CCDC 926557 (**2**) contain the supplementary crystallographic data for this Paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

§Dedicated to Prof. Dr. Phalguni Chaudhuri on the occasion of his 70th birthday.

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(3) The simulations of the experimental results indicated that a unique value for coupling constant J_{12}, J_{13}, and J_{23} (Figure 2, inset) cannot be achieved; that is, J_{12}, J_{13}, and J_{23} can be varied to reproduce the experimental result. In the case of **1** we observed Cu(II)-centered ground state, and that is why we chose antiferromagnetic coupling (J_{23} = −342.0 cm^{-1}) between two radical centers keeping J_{12} = J_{13} = 0.0 cm^{-1}. Because we had a radical-centered ground state we kept antiferromagnetic coupling between Cu and radicals higher than that of radicals.

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