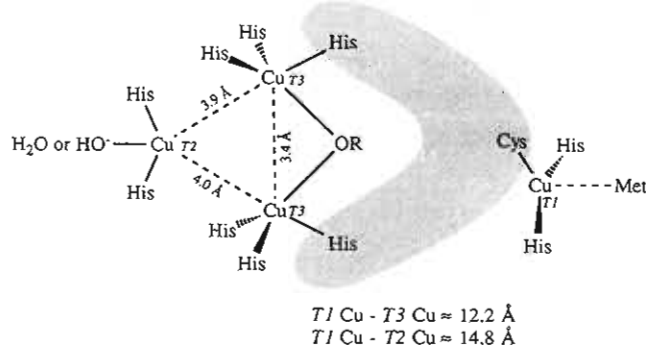


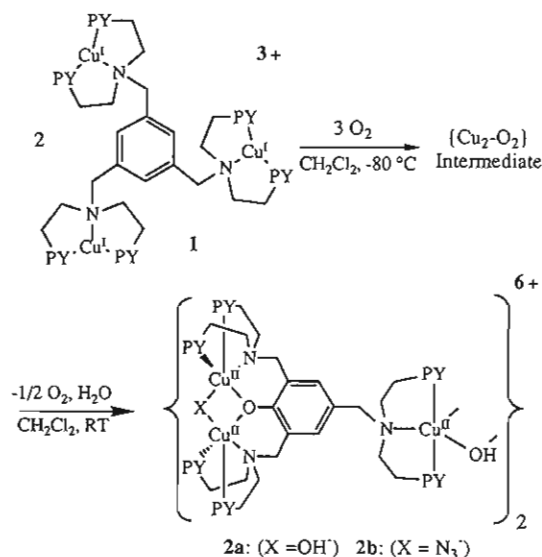
Communications

A Trinuclear Copper(I) Complex: Reaction with Dioxygen and the Formation of a Hexanuclear Copper(II) Cluster

Following our interest in the generation of $\{\text{Cu}_2\text{-O}_2\}^{\text{tr}}$ moieties as models for copper protein O_2 carriers (e.g. hemocyanin) and monooxygenases (e.g. tyrosinase),¹ we are currently expanding the scope of our studies to include the presence of a third (or fourth) copper(I) ion. Here, we report our initial attempts to develop new trinuclear copper(I) structural chemistry and examine $\text{Cu(I)}_3/\text{O}_2$ reactivity.² The impetus for this approach is the recent realization that "blue" multicopper oxidases contain such a unit. The copper ions in these proteins have previously been assigned by Malmström and co-workers as magnetically isolated type 1 (T1, "blue", high potential) and type 2 ("normal") and an EPR-silent coupled dinuclear pair (type 3).³ Solomon and co-workers⁴ first suggested that laccase actually possesses a trinuclear center, and a recent X-ray structural study by Messerschmidt and co-workers⁵ has confirmed the presence of such a cluster in the related protein ascorbate oxidase.^{5b} These and other biochemical studies suggest that substrates such as ascorbate reduce the T1 copper ion and electrons are then transferred to the Cu_3 cluster where the $4e^-/4\text{H}^+$ reduction of O_2 to H_2O is effected.



Scheme I



Ligand L (Scheme I, PY = 2-pyridyl) readily forms the trinuclear Cu(I) complex **1**.^{6,7} This reacts with O_2 at -80°C in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (9:1) to give the hexanuclear cluster **2a** (70%),⁸ in which L has been hydroxylated to L-O- (Scheme I) and whose structure has been confirmed by an X-ray crystallographic study of the azide analogue **2b**.⁹⁻¹¹ This molecule is centrosymmetric,

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- (5) (a) Messerschmidt, A.; Rossi, A.; Ladenstein, R.; Huber, R.; Bolognesi, M.; Gatti, G.; Marchesini, A.; Petruzzelli, R.; Finazzi-Agrò, A. *J. Mol. Biol.* **1989**, *206*, 513-529. (b) The X-ray analysis^{5a} indicates that a His-Cys-His peptide sequence is ligated to the T3 and T1 copper ions, as shown in the insert figure.

- (6) Isolated in >85% yield by the reaction of L with $\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4\text{PF}_6$. Data for $[\text{Cu}_3\text{L}(\text{PF}_6)_3] \cdot 2(\text{PF}_6)_3$ (**1**(PF_6)₃) are as follows. Anal. Calcd for $\text{C}_{51}\text{H}_{52}\text{Cu}_3\text{F}_{18}\text{N}_6\text{P}_3$: C, 43.09; H, 4.04; N, 8.86. Found: C, 43.02; H, 4.25; N, 8.50. IR (Nujol): $\nu(\text{PF}) = 840$ (s) cm^{-1} .
- (7) A related dinucleating *m*-xylyl ligand has been previously studied. In a reaction reminiscent of copper monooxygenases, its dicopper(I) complex is hydroxylated upon reaction with O_2 ; Karlin, K. D.; Gultneh, Y.; Hayes, J. C.; Cruse, R. W.; McKown, J.; Hutchinson, J. P.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 2121-2128.
- (8) Data for $[\{\text{Cu}_3(\text{L-O})(\text{OH})_2\}]_2(\text{PF}_6)_6 \cdot 2\text{H}_2\text{O}$ (**2a**(PF_6)₆) are as follows. Anal. Calcd for $\text{C}_{102}\text{H}_{120}\text{Cu}_6\text{F}_{36}\text{N}_{18}\text{O}_8\text{P}_6$: C, 41.15; H, 4.06; N, 8.47. Found: C, 40.63; H, 3.88; N, 8.27. IR (Nujol): $\nu(\text{OH}) = 3650$ (w), 3600 (w), $\nu(\text{PF}) = 840$ (s, br) cm^{-1} . UV-vis (CH_3CN): $\lambda_{\text{max}} = 345$ ($\epsilon = 2600$), 375 (2400), 647 (250) nm. $\mu_{\text{RT}} = 1.54 \mu\text{B}/\text{Cu}$. Λ_{m} (DMF) = $180 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Λ_{m} (CH_3CN) = $622 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. The results of Onsager plots in CH_3CN are also consistent with a 6:1 electrolyte formulation.^{15,16}
- (9) Generated by (a) the oxygenation reaction of **1** in the presence of NaN_3 or (b) a direct substitution reaction of **2a** with NaN_3 in CH_3CN . Data for $[\{\text{Cu}_3(\text{L-O})(\text{N}_3)(\text{OH})\}]_2(\text{PF}_6)_6$ (**2b**(PF_6)₆) are as follows. Anal. Calcd for $\text{C}_{102}\text{H}_{114}\text{Cu}_6\text{F}_{36}\text{N}_{24}\text{O}_4\text{P}_6$: C, 40.95; H, 3.84; N, 11.24. Found: C, 40.80; H, 3.80; N, 10.73. IR (Nujol): $\nu(\text{N}_3^-) = 2075$ (s), $\nu(\text{OH}) = 3600$ (w), $\nu(\text{PF}) = 830$ (s, br) cm^{-1} . UV-vis (CH_3CN): $\lambda_{\text{max}} = 375$ ($\epsilon = 2400$), 455 (2000), 665 (360) nm.

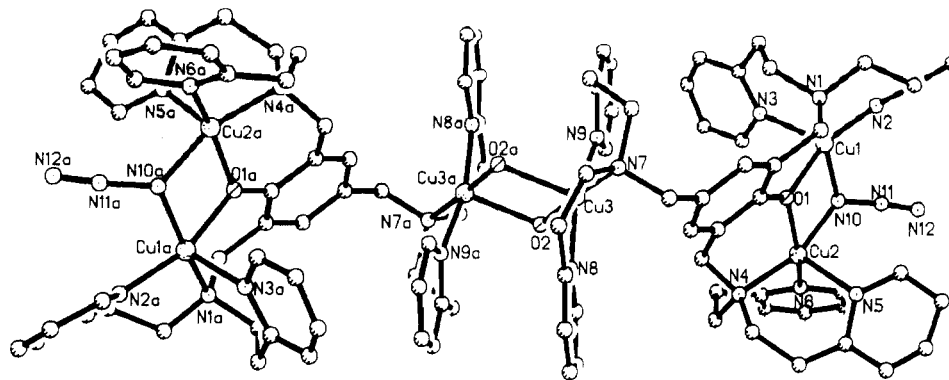


Figure 1. Perspective view of $[[\text{Cu}_3(\text{L}-\text{O})(\text{N}_3)(\text{OH})]_2]^{6+}$, showing the atom-labeling scheme. Selected bond lengths (\AA) and angles (deg) are as follows: Cu1...Cu2, 3.106 (1); Cu1...Cu3, 7.777 (2); Cu2...Cu3, 7.458 (3); Cu3...Cu3a, 3.119 (1); Cu1...Cu3a, 9.659 (3); Cu2...Cu3a, 10.130 (3); Cu1-O1, 1.964 (8); Cu1-N1, 2.053 (13); Cu1-N2, 1.982 (9); Cu1-N3, 2.196 (10); Cu1-N10, 1.953 (9); Cu2-O1, 1.971 (9); Cu2-N4, 2.021 (11); Cu2-N5, 2.163 (11); Cu2-N6, 1.976 (11); Cu2-N10, 1.954 (8); Cu3-O2, 1.914 (7); Cu3-O2a, 2.195 (11); Cu3-N7, 2.056 (11); Cu3-N8, 2.016 (9); Cu3-N9, 2.018 (9); O1-C1, 1.341 (12); N10-N11, 1.329 (7); N11-N12, 1.252 (1); O1-Cu1-N1, 92.9 (4); Cu1-O1-Cu2, 104.2 (3); Cu1-N10-Cu2, 105.3 (3); O1-Cu1-N10, 75.2 (3); O1-Cu2-N10, 75.1 (3); Cu3-O2-Cu3a, 98.4 (3); O2-Cu3-O2a, 81.6 (3).

consisting of two types of copper ion environments (Figure 1). Cu1 and Cu2 exist as a dinuclear Cu(II) pair with bridging phenoxo and μ -1,1-azido ligands. The third Cu(II) ion (Cu3) is pentacoordinated with near-planar ligation to the tridentate bis[2-(2-pyridyl)ethyl]amine (PY2) moiety and hydroxide (O2) ligand. There is a longer axial interaction with the O2a hydroxide ligand, which connects to the symmetry-related Cu3a atom and second trinuclear unit. Complexes **2a,b** contain elements of previously observed structures, i.e. doubly bridged (phenoxo and X^-) dinuclear units formed by hydroxylation of the *m*-xylyl dicopper(I) precursor,^{7,12} along with the "parallel-planar" $[\text{L}'\text{Cu}_3(\text{OH})_2\text{Cu}_3\text{aL}']^{2+}$ unit. The latter is known to be produced when three-coordinate Cu(I) complexes $[\text{L}'\text{Cu}^I]^+$ react with O_2 ($\text{Cu}:\text{O}_2 = 4:1$).^{13,14}

On the basis of EPR and conductance measurements, the hexanuclear structure **2a** is retained in CH_3CN and CH_2Cl_2 solution.^{8,17} In coordinating solvents such as DMF and MeOH, the $\text{Cu}_3\text{Cu}_3\text{a}(\text{OH})_2$ unit breaks, giving trinuclear units $[\text{Cu}_3(\text{L}-\text{O})(\text{OH})]^{3+}$. Conductance measurements in DMF give a 3:1 electrolyte formulation, and an EPR spectrum shows only a signal due to monomeric tetragonal Cu3 dicationic species, essentially unperturbed by the EPR-silent dibridged Cu1-Cu2 pair.

Low-temperature UV-vis (CH_2Cl_2) and manometric measurements ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$, 9:1) at -80°C shed some light on the course of the reaction of **1** with O_2 . Initially a brown intermediate with absorptions at 360 ($\epsilon \sim 20000$) and 435 nm forms, but within minutes this converts to a stable green species ($\lambda_{\text{max}} = 365$ nm, $\epsilon \sim 15000$), where the O_2 -uptake stoichiometry is $6:\sim 3 \text{ Cu}:\text{O}_2$. By analogy to dinuclear Cu(I) complexes containing alkane- and xyllyl-connected PY2 units,^{18,19} the results suggest that following the initial formation of an $\text{Cu}(\text{O}_2)\text{-Cu}$ adduct, hydroxylation occurs (at -80°C), giving the phenoxo- and OH-bridged Cu1-Cu2 part of **2a** ($\text{Cu}:\text{O}_2 = 2:1$).¹⁷ There is also an intermolecular $\text{Cu}(\text{O}_2)\text{-Cu}$ species formed with Cu3,¹⁴ accounting for the O_2 -uptake ratio observed. Warming of the green low-temperature $\{\text{Cu}_2\text{-O}_2\}$ intermediate results in a net disproportionation reaction, i.e. $2\{\text{Cu}(\text{O}_2)\text{-Cu}\} \rightarrow 2\{\text{Cu-O-Cu}\} + \text{O}_2$, consistent with the overall observed room-temperature O_2 uptake of $\text{Cu}:\text{O}_2 = 6:2.5$. Workup in the presence of some moisture would give the product **2a**, e.g. $\text{Cu-O-Cu} + \text{H}_2\text{O} \rightarrow \text{Cu}(\text{OH})_2\text{-Cu}$ (Scheme I).¹³

Although the presence of a third Cu(I) binding site in **1** does not appear to affect the O_2 reactivity of the other two copper ions, the results presented here show that $\text{Cu(I)}_3/\text{O}_2$ reactivity studies are feasible and that the hydroxylated ligand in **2** may allow for the generation or elaboration of better model systems. As in the copper oxidases, trinuclear complexes of L-O- contain two types of Cu environments, including a μ -OR-bridged dinuclear pair (e.g. T3). In kinetic studies on reactions of LCu^IX (L = N-donor, X = halide) with O_2 , Davies²⁰ has shown the third electron to be the key in the irreversible O-O reductive cleavage process, and a trinuclear copper(I) center therefore seems well suited to efficacious O_2 reduction.^{4,21} Investigation of $\text{Cu(I)}_n/\text{O}_2$ ($n = 3, 4$) reactions may also be relevant to the $4e^-/4\text{H}^+$ O_2 reduction occurring at the Fe-Cu dinuclear center in cytochrome *c* oxidase.^{21,22}

Acknowledgment. We thank the National Institutes of Health (K.D.K.; Grant GM 28962) for support of this research.

Supplementary Material Available: A drawing of hexacation **2b** with full labeling scheme and listings of crystal data and experimental conditions, atomic coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors (11 pages); a table of observed and calculated

- (10) X-ray-quality crystals of $[[\text{Cu}_3(\text{L}-\text{O})(\text{N}_3)(\text{OH})]_2(\text{PF}_6)_6 \cdot 4\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}]$ were obtained by recrystallization from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$. They were found to crystallize in the triclinic space group $P\bar{1}$ with $a = 11.284$ (3) \AA , $b = 12.212$ (3) \AA , $c = 25.865$ (9) \AA , $\alpha = 93.03$ (3) $^\circ$, $\beta = 95.26$ (3) $^\circ$, $\gamma = 112.13$ (2) $^\circ$, $V = 3273$ (2) \AA^3 , and $Z = 1$. A Nicolet R3m/V diffractometer was used in the ω -scan mode to collect 8852 unique reflections of which 5417 reflections with $F_o \geq 6\sigma(F_o)$ were used in the solution and refinement. The positional parameters of the copper atoms were determined by the Patterson method. The remaining non-hydrogen atoms were located on subsequent difference Fourier maps. Hydrogen atoms were calculated and fixed at 0.96 \AA from carbon. Anisotropic refinement was carried out on the copper atoms, oxygen atoms (O1-O3), solvent, nitrogen atoms (N1-N9, amine and pyridyl nitrogens; N10, azide nitrogen), and atoms in the anions; four molecules of lattice acetonitrile and one molecule of lattice H_2O per hexanuclear unit were identified and located in the final stages of refinement (some disorder is seen for one anion). The structure was refined to the current residual values of $R = 0.0893$ and $R_w = 0.1030$ (Mo $K\alpha$, $\lambda = 0.71073$ \AA).
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- (14) Monomeric three-coordinate Cu(I) complexes $[\text{L}'\text{Cu}^I]^+$, previously shown to react with O_2 ($\text{Cu}:\text{O}_2 = 4:1$ at 0°C) to give bis(μ -hydroxo)-bridged complexes like that containing Cu3 in **2**,¹³ also react at -80°C to give $\text{Cu}(\text{O}_2)\text{-Cu}$ species ($\text{Cu}:\text{O}_2 = 2:1$).¹⁵
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- (17) These phenoxo and X^- doubly bridged complexes are known to be EPR silent.^{7,12} Since a frozen-solution EPR spectrum of **2a** exhibits a weak $M_s = 2$ transition, the dimer structure $[-\text{Cu}_3(\text{OH})_2\text{Cu}_3\text{a}-]$ seen previously¹³ is indicated.

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structure factors (31 pages). Ordering information is given on any current masthead page.

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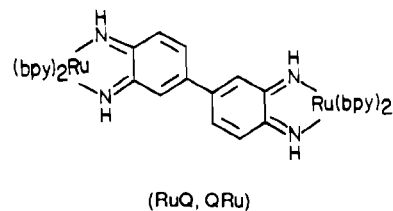
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Synthesis and Spectroscopic Characterization of Bis[bis(bipyridine)ruthenium(II)] 3,3',4,4'-Tetraimino-3,3',4,4'-tetrahydrobiphenyl and Its Redox Products

Our recent studies with ruthenium dioxolene species¹⁻⁵ have emphasized the extensive mixing between the ruthenium d orbitals and the dioxolene ligand molecular orbitals, mixing which can be tuned by altering the oxidation state of the complex. We report ruthenium complexes of 3,3',4,4'-tetraaminobiphenyl, forming dinuclear species, in a redox series, three members of which are described. The formation of conduction bands through polymeric versions of these complexes might allow for the construction of molecular wires, which could be switched by altering the oxidation state; this would alter the degree of conjugation in the pathway⁶ and/or control the angle of twist at the biphenyl ligand.

Much is known of electron transfer between two metals of different oxidation states via a bridging ligand.⁷⁻⁹ Less is known of electron transfer between ligands of different oxidation states.¹⁰⁻¹²

{[Ru^{II}(bpy)₂](3,3',4,4'-tetraimino-3,3',4,4'-tetrahydrobiphenyl)}(PF₆)₄ (bpy = 2,2'-bipyridine)^{13,14} isolated in this bis(quinone diimine) oxidation level is abbreviated (RuQ,QRu). The labels Q, SQ, and CAT refer to the successively reduced quinone diimine fragment. A mononuclear {[Ru^{II}(bpy)₂](3,4-diamino-3',4'-diamino-3,4-dihydrobiphenyl)}(PF₆)₂ species (RuQ,CAT) was also isolated.¹⁵



On the basis of studies of related mononuclear ruthenium quinonoid¹⁻⁴ and quinone diimine⁵ species, the electronic spectra (Figure 1) are assigned (Table I). Charge-transfer transitions occur from ruthenium to bipyridine and to the quinone diimine ligands in the spectra of both complexes (RuQ,QRu)¹⁶ and (RuQ,CAT). The oscillator strength of the Ru(II) → π* Q transition in the dinuclear species is almost twice that in the mononuclear species, but the Ru(II) → π* transition is substantially more narrow in the (RuQ,QRu) complex. This narrowness is indicative of a smaller reorganization contribution and, hence, less charge-transfer character in the excited state of (RuQ,QRu) than in that of (RuQ,CAT). Evidently the excited electron is spread over both quinone diimine fragments in this symmetric, albeit not strictly coplanar, biphenyl ligand.¹⁷ This species does not emit in fluid medium at room temperature, probably a consequence of internal redox quenching between the Ru → π* bpy MLCT state and the quinone diimine fragment.

Voltammetry of (RuQ,QRu) in acetonitrile shows two oxidation processes at 1.39 and 1.51 V (vs AgCl/Ag in CH₃CN) assigned to the formation of (Ru^{III}(Q···Q)Ru^{II}) and (Ru^{III}(Q···Q)Ru^{III}), respectively. There are four successive reductions of the biphenyl ligand (Figure 2) (-0.27, -0.49, -1.11, and -1.25 V vs AgCl/Ag), illustrating a series of mixed-valence products. Two more negative processes (-1.56 and -1.70 V) correspond with bipyridine reductions. The mononuclear species (RuQ,CAT) has two reduction processes generating (RuSQ,CAT) and (RuCAT,CAT) in acetonitrile at -0.485 and -1.12 V vs AgCl/Ag, respectively.

Controlled-potential reduction of (RuQ,QRu) in propylene carbonate, just negative of the first and second reduction couples, yields respectively (RuQ,SQRu), which may also be generated chemically by triethylamine reduction of (RuQ,QRu) and is stable indefinitely, and (RuSQ,SQRu), which shows slow decomposition that could not be overcome regardless of solvent.

Species (RuQ,SQRu) shows a free-radical ESR spectrum (g = 2.00, Δ_{pp} = 19 G, no hyperfine coupling to nitrogen, at 77 K),⁷ while (RuSQ,SQRu) is ESR-silent, at least to liquid-nitrogen temperature. The electron in (RuQ,SQRu) is evidently ligand-localized and the electronic structure is clearly different from the analogous (NH₃)₅Ru^{II}-(1,4-diimino-1,4-dihydrobenzene)-Ru^{III}(NH₃)₅ species with a metal-localized ESR spectrum.¹⁸

(RuQ,SQRu) shows the Ru(II) → π*(1) bpy electronic transition shifted to lower energy relative to (RuQ,QRu), since the overall positive charge on the ruthenium centers has been decreased. A Ru(II) → π* Q transition appears at essentially the same energy as that of the monomeric (RuQ,CAT) species. The Ru(II) → π* SQ transition, at 12 900 cm⁻¹, is shifted to the red of that observed in monomeric (RuSQ,CAT) but is substantially broader and more intense (Figure 3) (Table I). The higher energy

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- {[Ru(bpy)₂](3,3',4,4'-tetraimino-3,3',4,4'-tetrahydrobiphenyl)}(PF₆)₄ (I) (bpy = 2,2'-bipyridine) (RuQ,QRu), was prepared by refluxing Ru(bpy)₂Cl₂ (0.2 g) and 3,3',4,4'-tetraaminobiphenyl (0.044 g, Aldrich) in degassed methanol (25 mL) for 6 h. After the mixture was cooled to ambient temperature, several drops of concentrated ammonia and a solution of ammonium hexafluorophosphate (0.2 g) in water (2 mL) were added. The blood red solution was oxygenated for 45 min to develop a rich purple color. After solvent removal and trituration with methylene dichloride to remove a red impurity, the product was recrystallized from acetone.
- ¹H NMR: δ 12.08 (s, 2 H, imine), 11.98 (s, 2 H, imine), 8.50 (m, 8 H), 8.14 (m, 8 H), 7.62 (m, 8 H), 7.5 (m, 10 H), 7.38 (d, 2 H), 7.27 (d, 2 H). Anal. Calcd for C₃₂H₄₂F₂₄N₁₂P₄Ru₂: C, 38.7; H, 2.6; N, 10.4. Found: C, 39.2; H, 3.2; N, 9.9.

- {[Ru(bpy)₂](3,4-diamino-3',4'-diimino-3',4'-dihydrobiphenyl)}(PF₆)₂ (RuQ,CAT) (bpy = 2,2'-bipyridine): Ru(bpy)₂Cl₂ (0.1 g) and 3,3'-diaminobenzidine (0.088 g) were refluxed in degassed methanol (25 mL) for 24 h. The red-orange solution was exposed to air and filtered. The addition of several drops of concentrated ammonia changed the color to deep blue-purple. This solution was oxygenated for 6 h and then reduced in volume to 5 mL. Dropwise addition of an aqueous saturated solution of NH₄PF₆ provided blue microcrystals (0.15 g, 80%). Anal. C, H, N: ¹H NMR: δ 13.12 (s, 1 H, imine), 12.54 (s, 1 H, imine), 8.83 (m, 4 H), 8.25 (m, 4 H), 7.80 (m, 2 H), 7.43 (d, J = 9.44 Hz, 1 H), 7.26 (m, 4 H), 7.13 (m, 2 H), 7.05 (m, 1 H), 6.91 (m, 2 H), 6.59 (d, J = 8.25 Hz, 1 H), 6.52 (d, J = 6.5 Hz, 1 H), 5.23 (br s, 2 H, amine); 4.74 (br s, 2 H, amine).
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