

Unexpected Formation of a Cobalt(III) Phenoxazinylate Electron Reservoir

Frank D. Lesh,^[a] Richard L. Lord,^{*[a]} Mary Jane Heeg,^[a] H. Bernhard Schlegel,^[a] and Cláudio N. Verani^{*[a]}**Keywords:** Coordination chemistry / Redox-active ligands / Cobalt / Electrochemistry / Density functional calculations

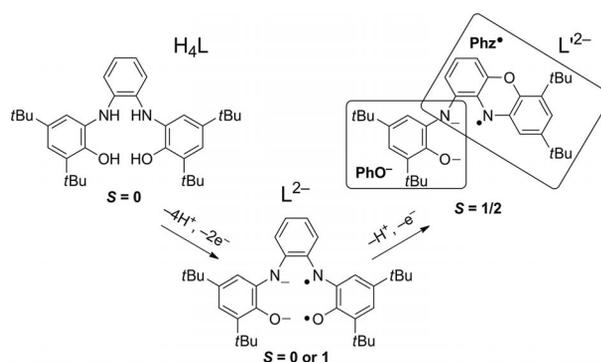
The redox-active ligand *N,N'*-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-phenylenediamine (H_4L), known for supporting catalytic processes with both late and early transition metals, unexpectedly undergoes an unusual and thus far unobserved cyclization. Upon equimolar treatment of a cobalt(II) salt in the presence of Et_3N under aerobic conditions, a ligand rearrangement occurs to afford an unprecedented

phenoxazinyl radical moiety (L'). The resulting bisligated Co complex, thoroughly characterized structurally and electronically and analyzed by multiple experimental and computational approaches, is presented. It is shown to traverse oxidation states from 2+ to 3-, spanning a thermodynamic window of approximately 2 V.

Introduction

There is considerable interest in the development and characterization of redox-active ligands with finely tuned potentials that act as electron reservoirs during catalytic processes.^[1] Among an ever growing group of such redox-active ligands, the species *N,N'*-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-diamine (H_4L) has received substantial attention.^[2–5] Coordination compounds with this ligand demonstrate catalytic behavior in pseudo-octahedral complexes with early transition metals and square-planar complexes with late transition metals. Such metal complexes mediate reductive bond formation^[3–5] and bioinspired aerobic oxidation,^[2] respectively, partially due to five ligand-based discrete oxidation levels. When complexed to metals, the most commonly observed ligand oxidation state is 2- ($H_4L \rightarrow L^{2-} + 4H^+ + 2e^-$, Scheme 1 left), which can be written with both closed shell^[2] and diradical electron configurations (only one shown). To the best of our knowledge, however, similar adducts with middle 3d metals (Mn, Fe, Co) have not received similar attention, despite the intriguing combination of this ligand with redox-rich metals.^[1,6–8] Towards this goal, we report here an unprecedented ligand transformation of L^{2-} whereby one of the phenolate/phenoxyl arms has cyclized to form a mixed phenolate/phenoxazinyl radical species, which we denote L'^{2-} ($L^{2-} \rightarrow L'^{2-} + H^+ + e^-$, Scheme 1 right).

Phenoxazines, found in nature as potent chromophores,^[9–11] demonstrate efficient electron transfer and high



Scheme 1.

luminescence quantum yields required for organic light-emitting diodes and dye-sensitized solar cells.^[12] Pierpont et al. observed a related transformation involving cyclization of a Schiff base biquinone ligand to confer a phenoxazinylate radical anion.^[13,14] Defining a ligand shorthand for this new ligand is complicated by the fact that the bridging amide can conjugate with both arms. In the past, there has been reference to imino and diimino catecholate/semiquinonate redox behavior when it was straightforward to group this nitrogen atom with a single arm of the ligand, phenolate or phenoxazinylate, respectively. We prefer to discuss the ligand as three fragments (Scheme 1, right): (i) the phenolate (PhO^- , left box), (ii) the bridging amide (N^- , overlap between boxes), and (iii) the phenoxazinyl radical (Phz' , right box). Thus, L'^{2-} is abbreviated PhO^-N^-Phz' . While this description is inherently too localized a description, it emphasizes correctly whether the phenoxazinyl or the phenolate arm is the major contributor to a given redox process.^[15] Herein, we describe the synthesis and characterization of the species $[Co(L')_2]^0$ along with its rich redox chemistry.

[a] Department of Chemistry, Wayne State University
5101 Cass Avenue, Detroit, MI 48202, USA
E-mail: cnverani@chem.wayne.edu
rllord@chem.wayne.edu

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Results and Discussion

Condensation of 3,5-di-*tert*-butylcatechol and *o*-phenylenediamine (2:1) together with Et₃N in *n*-heptane generates H₄L after four days of stirring at ambient temperature under aerobic conditions.^[2,4] Equimolar treatment of H₄L with anhydrous CoCl₂ in the presence of Et₃N under aerobic conditions in acetonitrile afforded a microcrystalline precipitate of [Co(L')₂]⁰. This stoichiometry does not seem to be affected by 1:1 vs. 2:1 H₄L/Co^{II} loadings or by the equivalents of added base (see Supporting Information). Dark green crystals suitable for X-ray analysis were obtained by slow evaporation from a CH₂Cl₂/CH₃CN mixture (1:1), and the unanticipated bisligated structure, in which each ligand is coordinated in a [O–N–N'] (O1–N1–N2/O3–N3–N4) meridional fashion, is presented in Figure 1. It is tempting to assign this neutral species as [Co^{II}(L'¹⁻)₂]⁰ on the basis of the fairly similar bond lengths within each of the two ligands (see Supporting Information); however, averaged metal–ligand bond lengths of 1.896 ± 0.004, 1.882 ± 0.006, and 1.955 ± 0.002 Å for Co–O, Co–N, and Co–N', respectively, strongly imply a low-spin cobalt(III) (^{LS}Co^{III}) metal center.^[16–18]

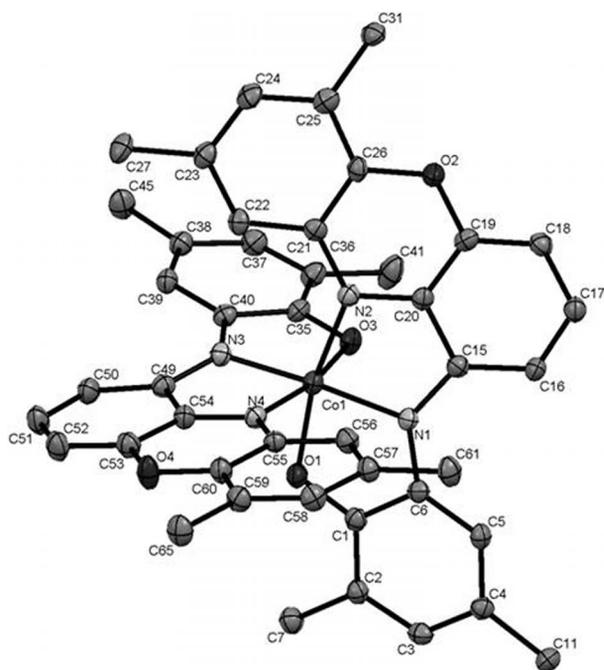


Figure 1. ORTEP diagram for [Co(L')₂]⁰·2MeCN showing 50% probability of the thermal ellipsoids. Solvent and hydrogen atoms are excluded, and the *t*Bu groups are truncated to the central quaternary carbon for clarity. Selected bond lengths (in Å) and angles (in °): Co1–N1 1.876(2), Co1–N3 1.887(2), Co1–O1 1.892(2), Co1–O3 1.899(2), Co1–N2 1.953(2), Co1–N4 1.956(2); N2–Co1–N3 104.83(8), N2–Co1–N4 92.64(8), O1–Co1–N3 86.55(7), O1–Co1–O3 91.35(7), O1–Co1–N1 84.80(7), O1–Co1–N4 89.33(7).

The formation of phenoxazinyl rings is known to occur in a basic, oxidizing medium for some aminocatechols.^[19] It is noteworthy that we have observed this ligand transformation in the presence of cobalt, but not manganese or iron ions, under similar basic, oxidizing conditions.^[20] One

plausible difference between these metals is that the Co^{II} ion is capable of reducing dioxygen to superoxide.^[21] Anaerobic mixing of H₄L and the cobalt salt affords the uncyclized metal–ligand adduct in a 2:1 ratio [Co^{II}(HL)₂]⁰, similar to the manganese species, as suggested by ESI mass spectrometric methods (see Supporting Information). Pursuit of mechanistic details and the possible role of superoxide are ongoing, but these are beyond the scope of this communication.

In order to understand the oxidation and spin states of the metal ion and ligands in the [Co^{III}(L')₂]⁰ species, we investigated multiple electronic structures with density functional theory (DFT) calculations.^[22] Two low-energy structures were identified, which are best described as a ^{LS}Co^{III} species with one unpaired electron, *S* = 1/2 (see Supporting Information for structural details and comparison to X-ray structure). One has ligands in different oxidation states, 2– and 1–, while the other is symmetric and has formal charges of 1.5– for each ligand. We present the former, because it does not invoke fractional electron charges, but it is important to note that these species are isoenergetic, which suggests that multiple resonance forms are accessible. A corresponding orbital analysis^[23] of this localized species suggests that one ligand is in the PhO[–]–N[–]–Phz' oxidation state with an unpaired *α* electron (Figure 2 top), while the other ligand is in the PhO[–]–N[–]–Phz' oxidation state with two antiferromagnetically (AF) coupled radicals (Figure 2 bottom). The overlap of the antiferromagnetically coupled orbitals is 0.8, which is quite large and may suggest a closed-shell description. However, all attempts to compute a structure with a closed-shell, localized 1– ligand collapsed to the delocalized structure with fractional ligand charges. The EPR-derived *g* value of 2.0 is consistent with the assignment of an organic radical, and despite the known shortcomings for predicting spin states of transition metal complexes a priori, DFT seems to capture correctly the physicochemical properties of [^{LS}Co^{III}(PhO[–]–N[–]–Phz')(PhO[–]–N[–]–Phz')]⁰.^[24,25]

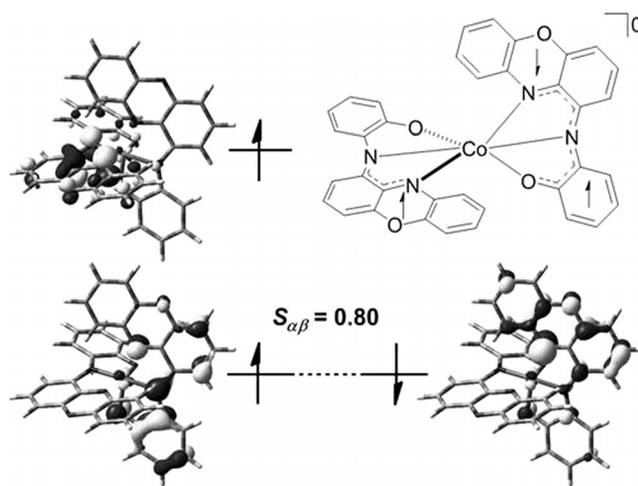


Figure 2. Contour plots (0.05 au) for the singly occupied (top) and AF coupled (bottom) orbitals resulting from the corresponding orbital analysis. *S*_{αβ} is the overlap integral for the AF coupled corresponding orbitals.

The unpaired electrons in the $\text{PhO}^-\text{N}^-\text{Phz}'$ and $\text{PhO}^-\text{N}^-\text{Phz}'$ ligands should demonstrate diagnostic intra- or interligand charge-transfer bands, and we therefore measured the absorption spectrum to probe further the electronic structure.

The UV/Vis spectrum of $[\text{L}^{\text{S}}\text{Co}^{\text{III}}(\text{PhO}^-\text{N}^-\text{Phz}')(\text{PhO}^-\text{N}^-\text{Phz}')]_2$ was collected in CH_2Cl_2 (see Figure 3). Prominent $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition bands positioned at 271 nm ($88770 \text{ L mol}^{-1} \text{ cm}^{-1}$) are succeeded by less intense shoulders at 387 and 474 nm (16630 and $9660 \text{ L mol}^{-1} \text{ cm}^{-1}$). Just beyond the visible region is a broad, low-energy band centered at 871 nm ($9690 \text{ L mol}^{-1} \text{ cm}^{-1}$). TD-DFT calculations corroborate the existence of a broad absorption feature around 1000 nm with an intensity of approximately $10000 \text{ L mol}^{-1} \text{ cm}^{-1}$, which comprises transitions mostly corresponding to intra- and interligand charge transfers.^[26] This assignment is consistent with earlier reports containing single and multiple phenoxazinylates^[11,27–28] and with our hypothesis of one or more ligand-based radicals.

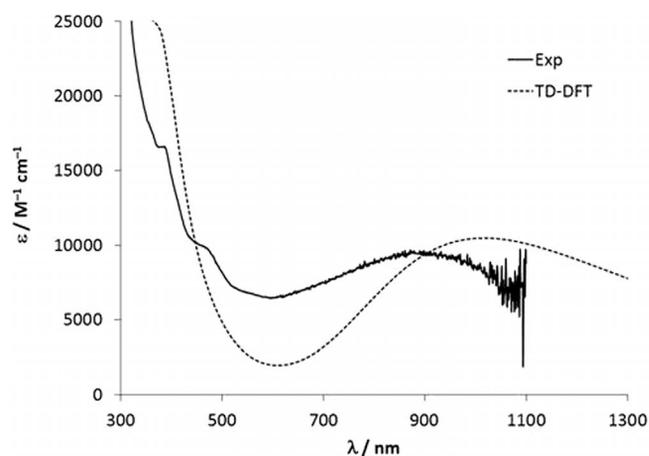


Figure 3. Experimental (solid) and simulated (dashed) UV/Vis absorption spectra of $[\text{L}^{\text{S}}\text{Co}^{\text{III}}(\text{PhO}^-\text{N}^-\text{Phz}')(\text{PhO}^-\text{N}^-\text{Phz}')]_2$ in CH_2Cl_2 .

Because the ligand can accommodate multiple oxidation levels in the ground state of the cobalt(III) complex, we investigated the redox behavior of $[\text{L}^{\text{S}}\text{Co}^{\text{III}}(\text{PhO}^-\text{N}^-\text{Phz}')(\text{PhO}^-\text{N}^-\text{Phz}')]_2$ by cyclic voltammetric methods in CH_2Cl_2 with TBA (tetra-*n*-butylammonium)PF₆ as supporting electrolyte. As Figure 4 demonstrates, five quasireversible electrochemical responses are observed between 800 and -1300 mV vs. Fc^+/Fc as the internal reference. The two redox couples at -1090 and -870 mV correspond to $\text{PhO}^-\text{N}^-\text{Phz}'/\text{PhO}^-\text{N}^-\text{Phz}'$ ^[27–29] and are consistent with the fact that the phenoxazinylate is more electron-rich than the phenolate in the fully reduced $\text{PhO}^-\text{N}^-\text{Phz}'$ state. The first two cathodic processes are followed at more positive potentials (-500 and -260 mV) by phenolate oxidation, $\text{PhO}^-\text{N}^-\text{Phz}'/\text{PhO}^-\text{N}^-\text{Phz}'$ ^[30–32] This description supports qualitatively the proposed electronic structure, which has two phenoxazinyl-based radicals and one phenoxyl-based radical. The redox process at 370 mV is presumably the formal oxidation of the amide ($\text{PhO}^-\text{N}^-\text{Phz}'/\text{PhO}^-\text{N}^-\text{Phz}'$), though the remaining charge may be quite delocalized.

One further oxidation is observed at 650 mV , though this process is highly irreversible and seems to correspond to the transfer of more than one electron. If correct, this scheme suggests that the $[\text{L}^{\text{S}}\text{Co}^{\text{III}}(\text{PhO}^-\text{N}^-\text{Phz}')(\text{PhO}^-\text{N}^-\text{Phz}')]_2$ complex can access oxidation states ranging from $2+$ to $3+$ with no metal-based redox events. We are currently pursuing a detailed experimental and computational characterization of the intermediate oxidation states within this redox series, aiming to compare them to the redox behavior of the manganese species with uncyclized ligands, $[\text{Mn}(\text{HL})_2]$.

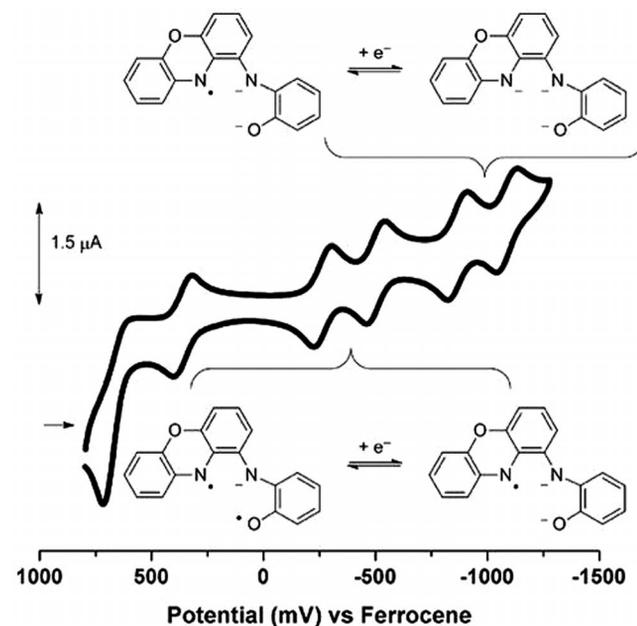


Figure 4. CV trace in CH_2Cl_2 , with 0.1 M TBAPF_6 , and $1.0 \times 10^{-3} \text{ M } [\text{L}^{\text{S}}\text{Co}^{\text{III}}(\text{PhO}^-\text{N}^-\text{Phz}')(\text{PhO}^-\text{N}^-\text{Phz}')]_2$, 150 mV s^{-1} ; mV vs. Fc^+/Fc . Insets are representations of the cathodic ligand redox events; only one resonance structure is shown for each.

Conclusions

In summary, we report a serendipitous functionalization of the redox-active ligand H_4L in the presence of a cobalt(II) salt, affording the new mixed phenoxazinylate/phenoxylate ligand L' . Multiple oxidation levels were accessible within this ligand when templated to a $\text{L}^{\text{S}}\text{Co}^{\text{III}}$ metal center in a 2:1 ratio, which DFT describes as $[\text{L}^{\text{S}}\text{Co}^{\text{III}}(\text{L}'^{-1})(\text{L}'^{-2})]$. We anticipate the rich redox chemistry exhibited by this bisligated complex, with five reversible, one-electron responses, to be an important electron reservoir motif towards our ultimate goal of multimetallic catalytic assemblies.

Experimental Section

H_4L was prepared as described by Chaudhuri et al.,^[2] by incorporating the purification steps recommended by Heyduk and co-workers,^[4] in approximately 50% overall yield.

Anhydrous CoCl_2 (0.130 g, 1 mmol) and Et_3N (0.2 mL) were added to a solution of H_4L (0.517 g, 1 mmol) in CH_3CN (25 mL), and the resultant mixture was heated at reflux for 1 h followed by stirring at ambient temperature for 4 h while exposed to air. A dark brown microcrystalline solid was collected by filtration and washed with CH_3CN . Yield: 40%. $\text{C}_{68}\text{H}_{86}\text{CoN}_4\text{O}_4$ (1082.4): calcd. C 75.18, H 8.35, N 5.16; found C 74.90, H 8.05, N 5.10. IR (KBr): $\tilde{\nu}$ = 2955, 2906, 2869 (vC–H, *t*Bu), 1528, 1479, 1457 (vC–O/vC–N, Phz/PhO) cm^{-1} . UV/Vis (CH_2Cl_2 , 1.0×10^{-3} M): λ (ϵ , $\text{L mol}^{-1} \text{cm}^{-1}$) = 271 (88770); 387 sh (16630), 474 sh (9660), 871 (9690). ESI⁺-MS (CH_2Cl_2): m/z (%) = 1082.61 (100%) [M + H]⁺.

Supporting Information (see footnote on the first page of this article): Materials and methods, syntheses, ORTEP drawings for [Co(L¹)(L²)], [Mn(HL)₂], and [Fe(L)Cl], EPR spectrum for [Co(L¹)(L²)], computational details (spin densities for doublets, Cartesian coordinates, frequencies, and energetics for computed structures, TD-DFT assignments).

Acknowledgments

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