

Both an Oxidation/Reduction Sequence and Deprotonation of a Unique Paramagnetic Ligand Lead to a Mixed-Valent Complex

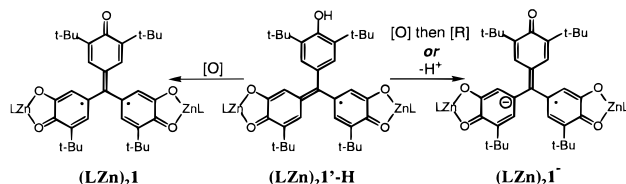
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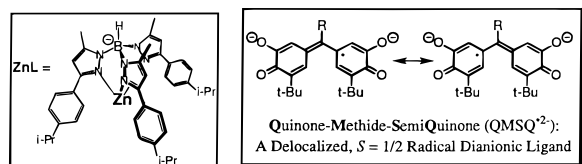
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Redox-active paramagnetic ligands are promising to play an increasing role in molecular magnetism,¹ valence tautomerism,^{2–5} and perhaps single-molecule magnets.^{6,7} In addition, cross-conjugated redox-active molecules are uniquely suited for correlating exchange coupling in biradical oxidation states⁸ with spin/charge delocalization in mixed-valent oxidation states.^{9–11}

Recently, we reported several redox-active, exchange-coupled bis(semiquinone)s^{12–15} and a few of their dinuclear metal complexes.^{16,17} One such bis(semiquinone) complex is $(\text{LZn})_2\mathbf{1}$, shown below ($\text{L} = \text{tris}(\text{cumenyl-methylpyrazolyl})\text{borate}$), prepared from



the unique complex $(\text{LZn})_2\mathbf{1}'\text{-H}$ by oxidation.¹⁶ The new radical dianionic ligand of $(\text{LZn})_2\mathbf{1}'\text{-H}$, Quinone-Methide-SemiQuinone



(QMSQ), is semiquinone-like and the unpaired electron and two negative charges are delocalized over both rings as illustrated above.¹⁸ Herein, we present the structure of $(\text{LZn})_2\mathbf{1}'\text{-H}$, and

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describe the spectroscopic and electrochemical changes that accompany its unusual conversion to a new mixed-valent anion $(\text{LZn})_2\mathbf{1}'^-$ and biradical $(\text{LZn})_2\mathbf{1}'$.

Complex $(\text{LZn})_2\mathbf{1}'\text{-H}$ was prepared as described previously,¹⁶ and the structure is shown in Figure 1 (cumenyl groups have been omitted for clarity). Selected geometric parameters are given in the Table 1 along with analogous values for semiquinone (SQ) and catecholate (Cat) complexes for comparison.^{19,20}

Complex $(\text{LZn})_2\mathbf{1}'\text{-H}$ is of approximate C_2 symmetry as a propeller-shaped conformation, with average dioxolene ring torsion angles of 22.6° and phenol ring torsion of ca. 38° relative to the plane made by atoms C4, C53, C99, and C100. The C4–C99 and C53–C99 bond lengths suggest delocalization between dioxolene rings.

Dioxolene bond lengths have been used as the structural criterion for distinguishing SQ from Cat.^{20b} Typical C–O bond lengths for SQ and Cat are 1.29 and 1.35 Å, respectively. As can be seen in Table 1, $(\text{LZn})_2\mathbf{1}'\text{-H}$ has two quite different C–O bond lengths: ca. 1.28 Å and ca. 1.32 Å. The shorter C–O bonds are para to C99 and are in accord with partial double bond character as demanded by the QMSQ formulation, while the longer C–O bonds are intermediate between those of SQ and Cat.

In addition to C–O bonds, C1–C6 bond lengths are also used to distinguish SQ (1.45 Å) from Cat (1.40 Å). From Table 1, the average value for $(\text{LZn})_2\mathbf{1}'\text{-H}$ is 1.50 Å—considerably longer than either SQ or Cat. In fact, the bond length pattern in the dioxolene rings confirms the quinoidal structure in $(\text{LZn})_2\mathbf{1}'\text{-H}$ (see Supporting Information), again consistent with the QMSQ formulation.

The phenol group imparts unique properties to $(\text{LZn})_2\mathbf{1}'\text{-H}$: H-atom abstraction gives a biradical,¹⁶ while deprotonation gives a mixed-valent anion. The electrochemical and spectroscopic manifestations of these transformations are shown in Figure 2.

The cyclic voltammogram (CV) of $(\text{LZn})_2\mathbf{1}'\text{-H}$ is shown in Figure 2A (top left), and consists of a single reversible one-electron reduction wave at -0.63 V vs Ag/AgNO_3 that we assign to the $(\text{LZn})_2\mathbf{1}'\text{-H}/(\text{LZn})_2\mathbf{1}'\text{-H}^-$ (QMSQ/QMCat) couple.

Figure 2B (middle left) shows the CV recorded after stirring $(\text{LZn})_2\mathbf{1}'\text{-H}$ with PbO_2 for 10 min to produce biradical $(\text{LZn})_2\mathbf{1}'$, and is comprised of two reversible reduction waves at -0.58 and

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(18) QMSQ is similar to a paramagnetic fluorone-derivative ligand reported by Dei and Gatteschi (Dei, A.; Gatteschi, D. *Inorg. Chim. Acta* **1991**, *189*, 125), however, this complex was not structurally characterized.

(19) A crystal of dimensions $0.24 \times 0.22 \times 0.12$ mm was mounted on a standard Siemens SMART CCD-based X-ray diffractometer equipped with a normal focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power (50 kV, 40 mA). The structure was solved and refined with the Bruker SHELXTL (version 5.10) software package (Sheldrick, G., Bruker AXS, Madison, WI, 1997). Formula, $\text{C}_{113}\text{H}_{134}\text{B}_2\text{N}_{12}\text{O}_5\text{Zn}_2$; formula weight 1892.68; crystal size (mm), $0.24 \times 0.22 \times 0.12$; temperature (K) = 158(2); crystal system, triclinic; space group, $P1$; $a = 14.6232(2)$ Å; $b = 16.143$ Å; $c = 25.0298(2)$ Å; $\alpha = 71.18^\circ$; $\beta = 75.70^\circ$; $\gamma = 77.23^\circ$; $V = 5354.57(8)$ Å³; $Z = 2$; $\mu = 0.505$ mm⁻¹; $D_{\text{calc}} = 1.174$ g/cm³; $F(000) = 2012$; reflections collected, 62248; no. of unique reflections, 20829; no. of parameters, 1317; $R = 0.055$; $wR2 = 0.135$. ($\Delta\rho$)_{max} = 0.892 e/Å³. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions. There is a slight disorder in part of the Tp ligand that was modeled by placing atoms at partial occupancy along with modest geometric restraints. Additional crystallographic results for $(\text{LZn})_2\mathbf{1}'\text{-H}$ are given in the Supporting Information.

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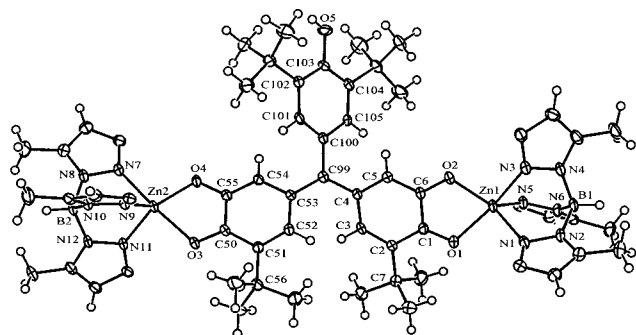


Figure 1. 50% ORTEP for $(\text{LZn})_2 1'\text{-H}$. Cumenyl groups have been omitted for clarity.

Table 1. Selected Geometric Parameters^a for $(\text{LZn})_2 1'\text{-H}$, Metal–Semiquinone Complexes (**MSQ**), and Metal–Catecholate Complexes (**MCat**)

structural parameter	$(\text{LZn})_2 1'\text{-H}$	MSQ	MCat
C1–O1	1.284(3)	1.270 ^b	1.35 ^c
C50–O3	1.276(3)		
C6–O2	1.314(3)	1.289 ^b	1.35 ^c
C55–O4	1.325(3)		
C1–C6	1.496(4)	1.462 ^b	1.40 ^c
C50–C55	1.503(4)		
C4–C99	1.473(4)		
C53–C99	1.442(3)		
dioxolene ring torsions	21.2(2), 24.0(2)		
phenol ring torsion	37.6(1)		

^a Bond lengths in Å, bond torsions in deg. ^b Average bond lengths; values are for 5-coordinate 3,5-di-*tert*-butylsemiquinone complexes taken from ref 20a. ^c Average bond lengths; values are for 6-coordinate 3,5-di-*tert*-butylcatecholate complexes taken from ref 20b.

–0.82 V with $\Delta E_{1/2} \approx 240$ mV. The first redox wave is for the $(\text{LZn})_2 1/(\text{LZn})_2 1^-$ (SQ–SQ/SQ–Cat) couple, while the second redox wave is for the $(\text{LZn})_2 1^-/(\text{LZn})_2 1^{2-}$ (SQ–Cat/Cat–Cat) couple, and the 240 mV wave splitting corresponds to a comproportionation equilibrium constant of ca. 10^5 . Thus, cross-conjugated $(\text{LZn})_2 1^-$ is best described as having a Class III (delocalized) mixed-valent dinuclear ligand.^{21,22}

Finally, $(\text{LZn})_2 1'\text{-H}$ was treated with an excess of potassium hydride, and the CV of the resulting anion is shown in Figure 2C (bottom left). As expected, this voltammogram is nearly identical with that in Figure 2B indicating that “deprotonated $(\text{LZn})_2 1'\text{-H}$ ” is part of the $(\text{LZn})_2 1/(\text{LZn})_2 1^-/(\text{LZn})_2 1^{2-}$ redox series. Thus, the mixed-valent anion can be created by either deprotonation of $(\text{LZn})_2 1'\text{-H}$ or one-electron reduction of $(\text{LZn})_2 1$, as indicated below.

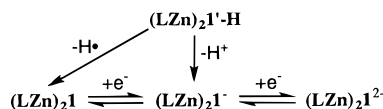


Figure 2 also shows the electronic absorption spectra for $(\text{LZn})_2 1'\text{-H}$ (D, top right), $\text{Na}^+(\text{LZn})_2 1^-$ (E, middle right), and $\text{K}^+(\text{LZn})_2 1^-$ (F, bottom right). Complex $(\text{LZn})_2 1'\text{-H}$ shows a unique NIR absorption band at 6870 cm^{-1} . Deprotonation of $(\text{LZn})_2 1'\text{-H}$ using potassium hydride to give $\text{K}^+(\text{LZn})_2 1^-$ results

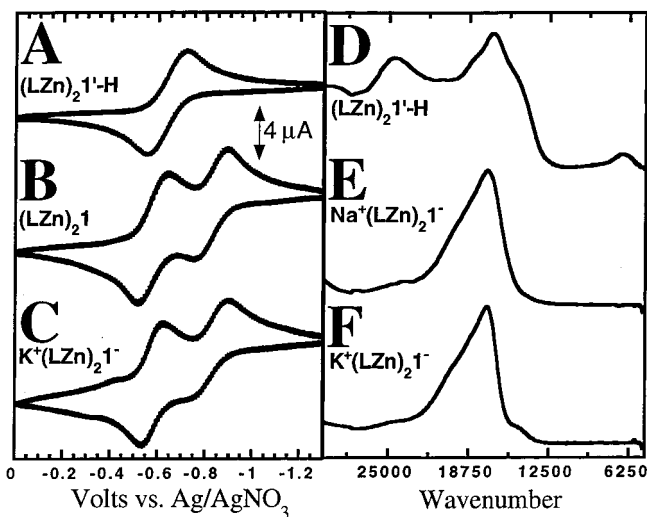


Figure 2. Cyclic voltammograms (left) for $(\text{LZn})_2 1'\text{-H}$ (A: top), $(\text{LZn})_2 1$ (B: middle), and $\text{K}^+(\text{LZn})_2 1^-$ (C: bottom; prepared by deprotonation of $(\text{LZn})_2 1'\text{-H}$) as ca. 1 mM solutions in THF. The supporting electrolyte is tetra-*n*-butylammonium hexafluorophosphate (400 mM). Scan rate = 50 mV/s. Electronic absorption spectra (right) for $(\text{LZn})_2 1'\text{-H}$ (D: top), $\text{Na}^+(\text{LZn})_2 1^-$ (E: middle; prepared by reduction of $(\text{LZn})_2 1$), and $\text{K}^+(\text{LZn})_2 1^-$ (F: bottom; prepared by deprotonation of $(\text{LZn})_2 1'\text{-H}$) as solutions in THF.

in the disappearance of the band at 6870 cm^{-1} , without the concomitant growth of a new band in the NIR region. The lack of a new band at lower energy supports our contention that $(\text{LZn})_2 1^-$ is a Class III mixed-valent ligand.²⁴ The mixed-valent species was also prepared by reduction of $(\text{LZn})_2 1$ with sodium amalgam²⁵ and the resulting spectrum is nearly identical with that of $\text{K}^+(\text{LZn})_2 1^-$ prepared by deprotonation of $(\text{LZn})_2 1'\text{-H}$, again demonstrating that $(\text{LZn})_2 1'\text{-H}$ can enter a redox series by either an oxidation/reduction sequence or deprotonation.

We have shown that the unique structure of a QMSQ ligand allows the preparation of a mixed-valent ligand through an oxidation/reduction sequence or by simple deprotonation. Further studies of our QMSQ ligand are underway.

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Supporting Information Available: Crystallographic data and figures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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 (23) The mixed-valent anion was prepared by mixing $(\text{LZn})_2 1'\text{-H}$ with an excess of KH (ca. 30-fold) followed by filtration through a Whatman filtration disk after a few seconds. Longer exposure times to KH increased the intensity of the small feature at ca. –0.4 V in the CV (Figure 2C) and the shoulder at ca. 15000 cm^{-1} in the visible region of the electronic spectrum (Figure 2F).
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 (25) To produce $\text{Na}^+(\text{LZn})_2 1^-$, biradical $(\text{LZn})_2 1$ was reduced with an excess of NaHg and the resulting bis(catecholate) complex was comproportionated with an equimolar amount of $(\text{LZn})_2 1$.