

Paramagnetic Zinc(II) Complexes of a Bis(catechol): Dependence of Product Spin State on Tautomerization of the Bis(catechol) Ligand

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We report the preparation and characterization of zinc(II) hydrotris(3-cumenyl-5-methylpyrazolyl)borate (**LZn**) complexes, (**LZn**)₂1'-H and (**LZn**)₂1, of a bis(catechol) ligand. The formation of (**LZn**)₂1'-H, an $S = 1/2$ complex, rather than (**LZn**)₂1, an $S = 1$ complex, is observed due to tautomerization of a reaction intermediate. The biradical complex, (**LZn**)₂1, can be prepared from (**LZn**)₂1'-H by oxidation, a conversion that is accompanied by a blue-green to red-purple color change and an increase in spin from $1/2$ to 1. The frozen solution EPR spectrum of the biradical complex (**LZn**)₂1 exhibits zero-field splitting and a $\Delta m_s = 2$ transition characteristic of a triplet state. The temperature dependence of the EPR signal intensity is consistent with high-spin coupling of the unpaired electrons of the ligand.

Introduction

In addition to preparing molecular magnets with ever-higher ordering temperatures, there is considerable interest in coupling magnetism to optical, redox, mechanical, and other properties. A central issue for designing such materials is identifying molecular fragments that trigger changes in magnetic properties upon irradiation with light, upon electron transfer, or as a consequence of a chemical reaction.^{1–24}

Transition metal complexes of semiquinones have been shown to exhibit numerous interesting electronic and exchange coupling properties.^{3,8,10,25–38} We recently reported the synthesis and characterization of several bis(semiquinone) ligands to be used for the construction of extended solids.^{39–42} Our biradical ligands

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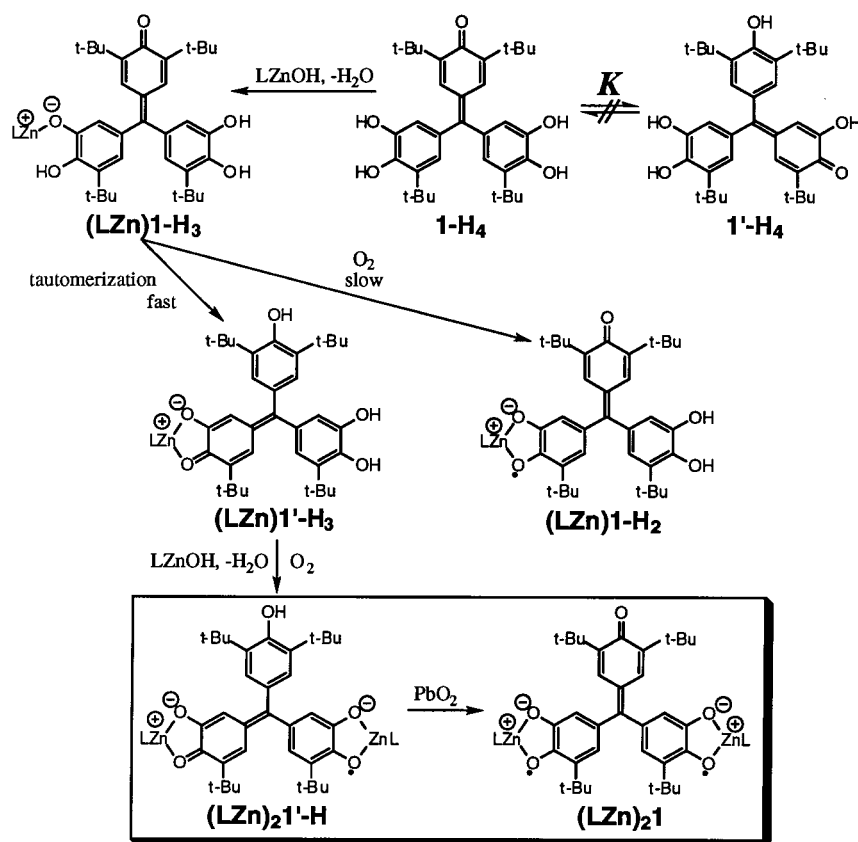
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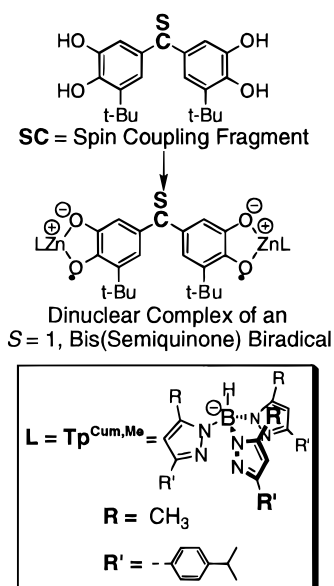
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Scheme 1



are designed to be ground-state triplets by virtue of the π -topologies of the spin coupling fragments (SC in the structures below).



In an effort to prepare metal complexes of our ligands and correlate molecular structure with spin-spin interactions, we found that these molecules form $S = 1$ complexes with zinc(II) hydrotris(3-*p*-cumenyl-5-methylpyrazolyl)borate (ZnL).⁴³ Since the ZnL species has an overall charge of +1, semiquinone complexes of this species are charge balanced.

One of our molecules, **1-H₄** (see Scheme 1), that has two

catechol groups linked to a quinonemethide fragment in a geminal fashion exhibits notably different coordination chemistry than other bis(catechols) we prepared. We report here the preparation and characterization of zinc(II) hydrotris(3-*p*-cumenyl-5-methylpyrazolyl)borate⁴⁴ (LZn) complexes, (LZn)₂1'-H and (LZn)₂1, of this ligand. Initially, the formation of (LZn)₂1'-H, an $S = 1/2$ complex, rather than (LZn)₂1, an $S = 1$ complex, is observed due to tautomerization of a reaction intermediate, (LZn)1-H₃. In addition, (LZn)₂1 can be prepared from (LZn)₂1'-H by oxidation, a conversion that is accompanied by a blue-green to red-purple color change and an increase in spin from $1/2$ to 1.

Results and Discussion

Our choice of coligand, L, is based on the recent work of Pierpont et al., who reported the synthesis of an analogous, stable 3,5-di-*tert*-butylsemiquinone (DBSQ) complex.⁴⁵ As shown in Scheme 1, the procedure used for synthesis of (LZn)₂1'-H is equivalent to that reported by Pierpont and consists of stirring a 1:1 methylene chloride/methanol solution of **1-H₄**⁴² with 2 equiv of LZnOH⁴⁴ in air. After 12 h, the product, a blue-green solid, was isolated by suction filtration. The room temperature magnetic moment of the blue solid is 1.7 μ_B , consistent with a single unpaired electron per complex.

The IR spectrum of (LZn)₂1'-H is devoid of C=O and broad O-H stretches of quinone or catechol functionalities, but exhibits a stretch near 1470 cm^{-1} in agreement with the presence of a semiquinone,²⁸ as well as a narrow stretch at 3635 cm^{-1} consistent with a non-hydrogen-bonded -OH group, like that of 2,6-di-*tert*-butylphenol.

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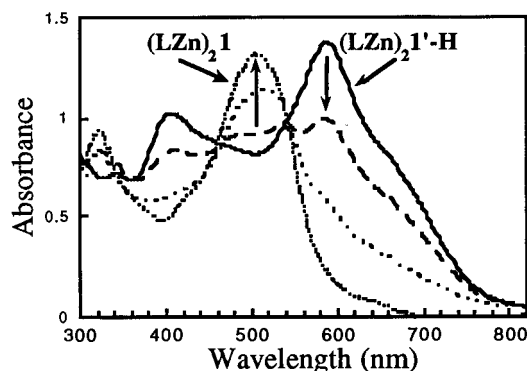


Figure 1. UV-visible spectra recorded during the oxidation of $(\text{LZn})_2\mathbf{1}'\text{-H}$ with PbO_2 in THF solvent. Isosbestic points are visible near 344, 460, and 540 nm.

The fluid-solution EPR spectrum of $(\text{LZn})_2\mathbf{1}'\text{-H}$ recorded at 298 K exhibits unresolved hyperfine structure, while the frozen-solution (77 K) EPR spectrum consists of a single line with a peak-to-peak width of ca. 7 G.⁴⁶ Thus, the spectroscopic observations are consistent with an $S = 1/2$ radical complex. To our knowledge, this is the first report of a dinuclear complex of a paramagnetic ligand like that in $(\text{LZn})_2\mathbf{1}'\text{-H}$.

Reactions carried out in neat methylene chloride also gave $(\text{LZn})_2\mathbf{1}'\text{-H}$, indicating the lack of a significant solvent-dependent tautomerism of $\mathbf{1}\text{-H}_4$ to $\mathbf{1}'\text{-H}_4$ as indicated in Scheme 1. In fact, ^1H NMR spectra of the ligand in both d_4 -methanol and d_2 -methylene chloride exhibit signals characteristic of only $\mathbf{1}\text{-H}_4$: no signals for the less-symmetric form $\mathbf{1}'\text{-H}_4$ are observed.⁴⁶ Thus, the formation of the $S = 1/2$ complex is consistent with monodentate complexation followed by tautomerization and subsequent formation of $(\text{LZn})\mathbf{1}'\text{-H}_3$ being faster than either oxidation (which should give some $(\text{LZn})_2\mathbf{1}$) or coordination of a second zinc ion (which should also lead to $(\text{LZn})_2\mathbf{1}$), as shown in Scheme 1.

Exposure of a THF solution of $(\text{LZn})_2\mathbf{1}'\text{-H}$ to PbO_2 results in a color change from blue-green to red-purple, yielding $(\text{LZn})_2\mathbf{1}$. This compound has a room temperature magnetic moment of $2.6 \mu_B$, slightly greater than the value expected for two unpaired electrons ($2.45 \mu_B$). The oxidation can be followed by electronic absorption spectroscopy as shown in Figure 1. Isosbestic points are observed near 344, 460, and 540 nm.

The IR spectrum of $(\text{LZn})_2\mathbf{1}$ lacks the $-\text{OH}$ stretch at 3635 cm^{-1} exhibited by $(\text{LZn})_2\mathbf{1}'\text{-H}$. The fluid-solution EPR spectrum of $(\text{LZn})_2\mathbf{1}$ recorded at 298 K consists of a single line with a peak-to-peak width of ca. 3 G. However, as shown in Figure 2, the frozen-solution EPR spectrum recorded at 77 K in 2-methyltetrahydrofuran exhibits fine structure characteristic of a triplet state.^{47–49} Also observable near half-field is a $\Delta m_s = 2$ transition (inset). Both of these observations are consistent with an $S = 1$ bis(semiquinone) biradical complex. Simulation⁵⁰ of the $\Delta m_s = 1$ region of the EPR spectrum gives zero-field-splitting parameters $|\mathbf{D}/hc| = 0.0093 \text{ cm}^{-1}$ and $|\mathbf{E}/hc| = 0.0006 \text{ cm}^{-1}$, values close to those of the bis(semiquinone) prepared by bulk electrolysis.⁴² Finally, as shown in Figure 3, the intensity

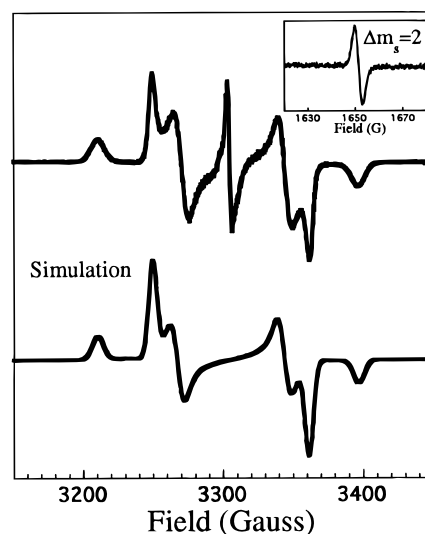


Figure 2. X-band EPR spectra of biradical complex $(\text{LZn})_2\mathbf{1}$ as a solution in 2-methyltetrahydrofuran at 77 K (top); simulation (bottom), using $|\mathbf{D}/hc| = 0.0093 \text{ cm}^{-1}$ and $|\mathbf{E}/hc| = 0.0006 \text{ cm}^{-1}$, $g_{xx} = g_{yy} = 2.00232$, and $g_{zz} = 2.00350$. Inset: $\Delta m_s = 2$ region.

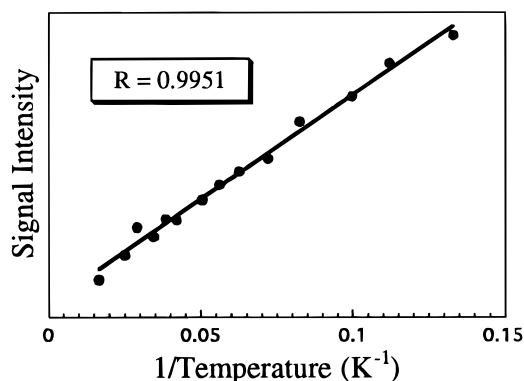


Figure 3. Curie plot for doubly integrated $\Delta m_s = 2$ transition. Temperature range: 7–60 K.

of the EPR signal (doubly integrated $\Delta m_s = 2$ transition) varies linearly with inverse absolute temperature, consistent with high-spin coupling of the unpaired electrons of the ligand.⁵¹

Conclusions

In conclusion, we have presented the synthesis and spectroscopic characterization of a new $S = 1/2$ radical complex, $(\text{LZn})_2\mathbf{1}'\text{-H}$. This complex can be easily oxidized to an $S = 1$ bis(semiquinone) species, which has also been characterized spectroscopically. The oxidation reaction consists of loss of a hydrogen atom from the phenol group of the ligand and is accompanied by a color change from blue-green to red-purple. The frozen-solution EPR spectrum of the biradical complex $(\text{LZn})_2\mathbf{1}$ exhibits zero-field splitting and a $\Delta m_s = 2$ transition characteristic of a triplet state. The temperature dependence of the EPR signal intensity is consistent with high-spin coupling of the unpaired electrons of the ligand.

Efforts toward structural characterization of $(\text{LZn})_2\mathbf{1}'\text{-H}$ and $(\text{LZn})_2\mathbf{1}$ and variable-temperature magnetometry studies of $(\text{LZn})_2\mathbf{1}$ are underway.

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Experimental Section

Unless noted otherwise, reactions were carried out in oven-dried glassware under an argon atmosphere. Methylene chloride and 2-methyltetrahydrofuran were distilled from CaH_2 under nitrogen. THF was distilled from sodium benzophenone/ketyl prior to use. Methanol was used as received from Fisher Scientific. Other chemicals were purchased from Aldrich Chemical Co. NMR spectra were recorded on a Varian spectrometer at 300 MHz for ^1H NMR either using deuteriomethanol as solvent and referenced to protiomethanol at 3.34 ppm or using deuteriomethylene chloride as solvent and referenced to protiomethylene chloride at 5.32 ppm. Elemental analysis was performed by Atlantic Microlab, Inc., Norcross, GA. IR spectra were recorded on a BioRad FTS-6000 spectrophotometer, and samples were films formed by the evaporation of methylene chloride or THF solutions on a NaCl plate. Electronic absorption spectra were recorded on a Hewlett-Packard model 8452A spectrophotometer. Magnetic moments were obtained from a Cahn Faraday balance, calibrated with $\text{Hg}[\text{Co}(\text{SCN})_4]$. X-band EPR spectroscopy was performed using an IBM-Brüker E200SRC spectrometer. Variable temperature EPR (VT-EPR) experiments were performed using an Oxford model 900 liquid helium cryostat. Signal saturation experiments were performed to ensure that the concentration and gain/modulation settings gave signal responses that were a linear function of $1/\text{attenuation}$. Solutions for EPR and VT-EPR experiments were prepared in a Vacuum Atmospheres glovebox under a nitrogen atmosphere, using solvents that had been distilled as above and subjected to several freeze-pump-thaw cycles.

Complex $(\text{LZn})_2\mathbf{1}'\text{-H}$. A flask containing $\mathbf{1}\text{-H}_4$ (30 mg, 55 mmol), LZnOH (76 mg, 110 mmol), and 15 mL of 1:1 methanol/ CH_2Cl_2 was stirred overnight. The blue-green solid was filtered off and air-dried to give 73 mg, 70% yield. IR (film): ν_{max} 3635 (w), 3066 (w), 2963, 2543, 1562, 1525, 1478, 1441, 1366, 1179, 1057, 833, 786 cm^{-1} . Anal. Calcd for $\text{C}_{113}\text{H}_{134}\text{B}_2\text{N}_{12}\text{O}_5\text{Zn}_2$: C, 71.70; H, 7.13; N, 8.88. Found: C, 71.40; H, 7.15; N, 8.86.

Complex $(\text{LZn})_2\mathbf{1}$. A flask containing $(\text{LZn})_2\mathbf{1}'\text{-H}$ (20 mg, 10.6 μmol) and PbO_2 (24 mg, 100 μmol) in THF (5 mL) was stirred in the dark for 2 h. The red-purple reaction mixture was filtered through a plug of Celite, and the solvent was removed in vacuo to yield 20 mg, 100% of a red-purple solid. IR (film): ν_{max} 3057 (w), 2963, 2543, 1562, 1525, 1478, 1441, 1357, 1179, 1056, 834, 787 cm^{-1} . MS: $\text{C}_{113}\text{H}_{133}\text{B}_2\text{N}_{12}\text{O}_5\text{-Zn}_2$ calcd mass 1892.94, obsd 1892.97.

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Supporting Information Available: Spectral data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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