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Structural and Spectroscopic Characterization of a Zinc-bound *N*-oxy-phthalimide Radical

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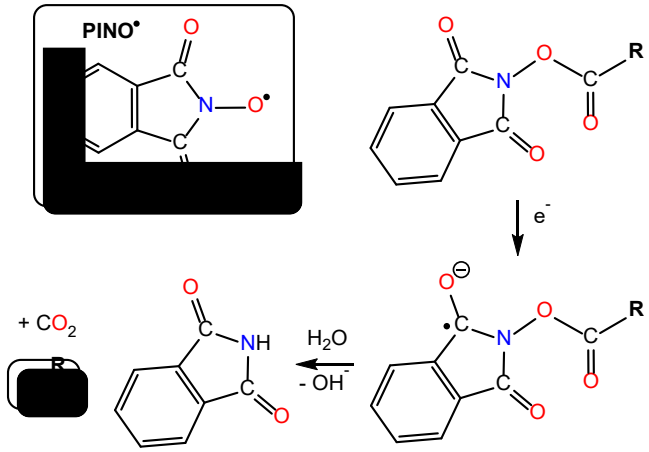
ABSTRACT: Thermolysis of a 1:1:1 mixture of ^{Me}LH (^{Me}L = {(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(Me)}$_2$CH), *N*-hydroxyphthalimide (HOPth), and ZnEt$_2$ in toluene at 77 °C provided [^{Me}LZn(OPth)] (**1**) in good yield after work-up. Subsequent reduction of **1** with 1.3 equiv of KC$_8$ and 1 equiv of 2.2.2-cryptand, in THF, provided [K(2.2.2-cryptand)][^{Me}LZn(OPth)] (**2**) in 74 % yield after work-up. Characterization of **2** via X-ray crystallography and EPR spectroscopy reveals the presence of an $S = 1/2$ radical on the *N*-oxy-phthalimide ligand. Importantly, these data represent the first structural and spectroscopic confirmation of the redox activity of a metal-bound *N*-oxy-phthalimide fragment, expanding the range of structurally characterized redox-active ligands.

The utility of *N*-hydroxyphthalimide (HOPth) and its derivatives in synthetic chemistry has been well established over the past two decades.[1-5] For example, the highly reactive phthalimide *N*-oxyl radical (i.e., PINO•; Scheme 1, inset), which is generated from HOPth *in situ*, can oxidize a variety of organic substrates, including lignin model compounds,[6] cycloalkanes,[7-11] alkenes,[12-15] and alcohols,[16-19] as well as a wide variety of benzylic compounds,[20-26] under both metal-free and metal-assisted conditions. *N*-(acyloxy)phthalimides and *N*-alkoxyphthalimides have also found widespread use, specifically as convenient sources of alkyl radicals.[5, 27] This approach was pioneered by Okada and co-workers, who demonstrated that *N*-(acyloxy)phthalimides could cross-couple with electron-deficient olefins under photocatalytic conditions.[28, 29] The proposed mechanism involves a photo-initiated reduction of the *N*-(acyloxy)phthalimide to form a radical anion, which subsequently undergoes decarboxylation and formation of an alkyl radical (Scheme 1), which is then trapped by substrate.



Scheme 1. Proposed mechanism of alkyl radical generation from *N*-(acyloxy)phthalimide. Inset: molecular structure of phthalimide *N*-oxyl radical (PINO•).

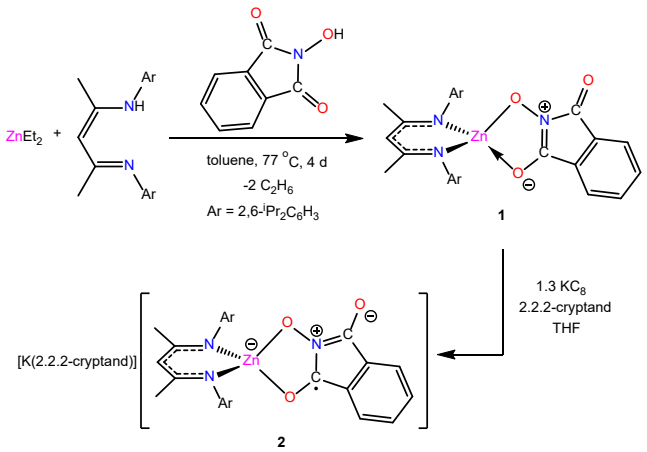
This method of alkyl radical generation has since been widely adopted,[5, 30] and includes examples of its use in alkylation,[31-33] aminylation,[34, 35] alkoxylation,[36] borylation,[37, 38] indenylation,[39] arylation,[40] and alkenylation.[30, 41, 42] This methodology has also been incorporated into the synthesis of complex natural products.[43-45] These transformations are often metal-catalyzed, and while the proposed catalytic cycles do not typically invoke L$_n$M(OPth) complex formation, it seems reasonable that electron transfer to the phthalimide group could occur via an inner sphere mechanism. However, our structural understanding of metal *N*-oxy-phthalimide complexes is limited. Indeed, only a handful have been structurally characterized, including [(*n*-Bu$_3$P)Ag(OPth)]$_2$,[46] [Cr(N)(OPth)(N^{i}Pr$_2$)$_2$],[47] and [Sb(OPth)$_2$Ph$_3$].[48] More importantly, to our knowledge, there are no reported structurally characterized examples of the OPth radical species, which hampers our understanding of the mechanism of decarboxylation and potentially limits the further development of this chemistry.

Nonetheless, our general understanding of redox non-innocent ligands has grown significantly in recent years.[49-56] Complexes with redox non-innocent ligands have proven useful in catalysis, where the non-innocent ligands function as electron reservoirs, allowing first row transition metals to easily perform multi-electron transformations.[57] Redox non-innocent ligands can also enable multi-electron chemistry in the actinides,[58-60] and they play an important role in biology.[61]

Previously, we reported on the synthesis and reactivity of a series of metal complexes containing the redox-active TEMPO ligand, including [FeCl$_3$(η^1-TEMPO)] (TEMPO = 2,2,6,6-tetramethylpiperidine-*N*-oxide), [AlX$_3$(η^1-TEMPO)] (X = Cl, Br), and [(η^1-TEMPO)$_2$BBr].[62-64] In these examples, the TEMPO moiety was bound to the metal ion in both its radical and anionic forms. Building on this work, we have

now prepared a novel β-diketiminate-supported[65] Zn phthalimide *N*-oxide complex, which allowed us to explore the redox activity of the phthalimide fragment, using both structural and spectroscopic techniques.

Heating a 1:1:1 mixture of ^{Me}LH (^{Me}L = {(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(Me)}$_2$CH), HOPth, and ZnEt$_2$ in toluene at 77 °C for 4 d produced a bright orange suspension. Work-up of this reaction mixture provided [^{Me}LZn(OPth)] (**1**) in 77% isolated yield (Scheme 2, top).



Scheme 2. Syntheses of complexes **1** and **2**.

Complex **1** crystallizes with two independent molecules in the asymmetric unit as the Et$_2$O solvate, **1**·1.5Et$_2$O. It features a tetrahedral Zn^{2+} center, wherein the OPth ligand adopts a bidentate *O*,*O*-κ^2 coordination mode (Figure 1; crystallographic data are given in the SI, Table S1). The metrical parameters of the two molecules within the asymmetric unit are very similar, and the parameters of only one will be discussed in detail. Not surprisingly, the Zn–O distance of the *N*-bound oxygen atom (Zn1-O2 = 1.979(2) Å; Figure 2) is shorter than the Zn–O distance of the *C*-bound oxygen atom (Zn1-O1 = 2.088(2) Å), reflecting the greater anionic character of O2. Additionally, the C–O distance of the Zn-bound carbonyl group is longer (C30–O1 = 1.246(3) Å) than the C-O distance of the free carbonyl (C31-O3 = 1.208(4) Å), consistent with activation of the C=O fragment upon ligation to Zn^{2+}. The phthalimide N–C distances in **1** are also inequivalent (i.e., N3–C31 = 1.414(4) Å and N3–C30 = 1.353(3) Å). Overall, these metrical parameters suggest the presence of localized π-bonds between N3 and C30 and between O3 and C31, as drawn for **1** in Scheme 2. Consistent with this suggestion, the sum of interatomic angles around N3 is 359.9°, as expected for an sp^2-hybridized nitrogen. For comparison, the C–O distances in free HOPth are equivalent (1.210(5) and 1.214(5) Å; Figure 2). The N-C distances in free HOPth are also equivalent (1.384(6) and 1.397(6) Å). Both observations are consistent with a delocalized electronic structure in HOPth, in contrast to the situation for **1**.

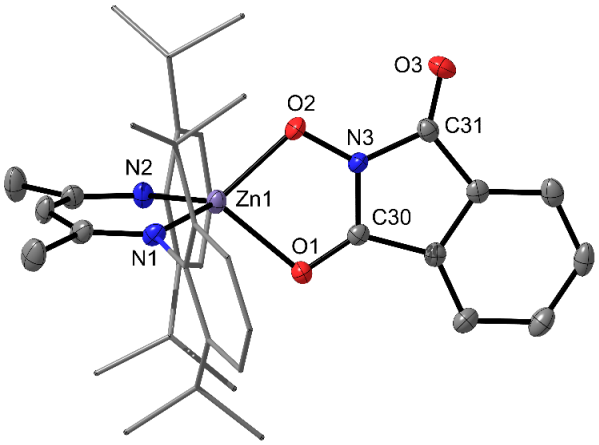


Figure 1. Solid-state structure of **1**·1.5Et$_2$O. Thermal ellipsoids set at 50% probability. Et$_2$O solvate molecules and hydrogen atoms omitted for clarity. *N*-aryl substituents shown in wireframe.

To our knowledge, the *O*,*O*-κ^2 *N*-oxy-phthalimide binding mode observed in **1** is unique. For comparison, [(*n*-Bu$_3$P)Ag(OPth)]$_2$ and [Sn$_4$O$_2$Me$_8$Cl$_2$(OPth)$_2$] exhibit *O*-κ^1:μ binding modes of their phthalimide ligands,[46, 66] whereas [Cr(N)(OPth)(N^{i}Pr$_2$)$_2$] and [Sb(OPth)$_2$Ph$_3$] exhibit *O*-κ^1 binding modes.[47, 48] Interestingly, in these examples the *N*-oxy-phthalimide group maintains its delocalized electronic structure. For example, [(*n*-Bu$_3$P)Ag(OPth)]$_2$ exhibits indistinguishable N–C distances (1.389(1) and 1.397(1) Å) and indistinguishable C–O distances (1.219(1) and 1.213(1) Å).

The ^{1}H NMR spectrum of complex **1** in C$_6$D$_6$ features doublets at 6.77 and 6.47 ppm, which are assignable to the two unique C-H environments on the *N*-oxy-phthalimide ligand (Figure S1). Likewise, the spectrum features doublets at 1.53 and 1.20 ppm, which are assignable to the two diastereotopic isopropyl CH$_3$ environments of the *N*-aryl substituents of the β-diketiminate ligand. Both observations are diagnostic of a C_{2v}-symmetric complex, which contrasts with the C_s symmetry observed in the solid-state. This discrepancy can be rationalized by invoking rapid exchange of the Zn-ligated carbonyl group (O1 in Figure 1) with the unligated carbonyl group (O3). Alternatively, the OPth ligand may adopt an η^1 coordination mode in solution, as is observed for [Cr(N)(OPth)(N^{i}Pr$_2$)$_2$] and [Sb(OPth)$_2$Ph$_3$].[47, 48] The IR spectrum of **1** (KBr pellet) features ν$_{CO}$ modes at 1793 and 1766 cm^{-1} (Figure S9). For comparison, free HOPth features ν$_{CO}$ modes at slightly higher energies (1833 and 1782 cm^{-1}), consistent with the weakening expected upon ligation.[67] Finally, the cyclic voltammogram of **1** in THF reveals a reversible oxidation feature at −1.84 V (vs Fc/Fc$^+$; Figure S13), which we attribute to the reduction of the *N*-oxy-phthalimide ligand.

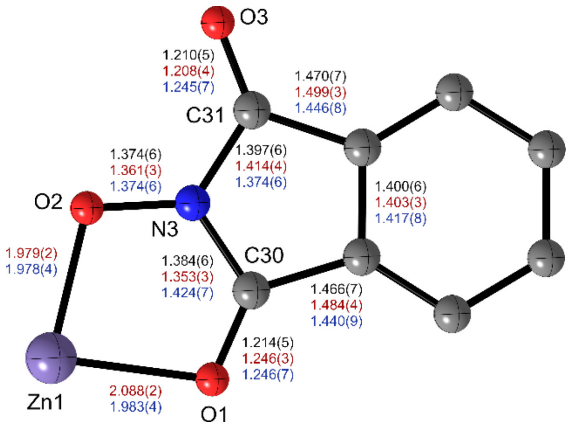


Figure 2. Bond distance (Å) comparison for free HOPth (black), **1**·1.5Et$_2$O (red), and **2** (blue). Carbon atoms shown in gray, oxygen atoms shown in red, nitrogen atom shown in blue, and zinc atom shown in lavender. Structure shown is that of **1**. Metrical parameters for HOPth taken from Ref [68].

The cyclic voltammogram of **1** suggested that its 1e$^-$ reduction product could be isolable. Gratifyingly, reaction of **1** in THF with 1.3 equiv of KC_8, in the presence of 2.2.2-cryptand, quickly produced a deep olive green solution. Work-up of the reaction mixture permitted isolation of [K(2.2.2-cryptand)][^{Me}LZn(OPth)] (**2**) in 74% yield (Scheme 2, bottom). Consistent with the anticipated paramagnetism, the signals in its ^{1}H NMR spectrum are extremely broad (Figure S3). In particular, a broad resonance at 5.11 ppm is assignable to the γ-CH position of the β-diketiminate ligand, whereas broad resonances at 2.04 and 1.35 ppm are assignable to its diastereotopic isopropyl CH_3 groups of the *N*-aryl substituents. Additionally, we observe broad resonances at 3.17 and 2.23 ppm, which are assignable to the 2.2.2-cryptand moiety. Finally, the IR spectrum of **2** (KBr pellet) features a ~100 cm^{-1} redshift of its ν_{CO} modes relative to **1** (Figure S10), consistent with the expected decrease in the C=O bond order upon reduction.

Complex **2** was also characterized by X-ray crystallography. It crystallizes in the triclinic space group *P*-1 as a discrete cation/anion pair (Figure S8). As was observed for **1**, its OPth ligand is bound in a *O*,*O*-κ^2 fashion to the tetrahedral Zn^{2+} center. Additionally, the Zn–O distance of the *N*-bound oxygen atom (Zn1-O2 = 1.978(4) Å; Figure 2) is indistinguishable to that observed for **1** by the 3σ criterion. In contrast, however, the Zn–O distance of the *C*-bound oxygen atom in **2** (1.983(4) Å) is considerably shorter (Figure 2). Moreover, the two C-O distances in **2** are within error (1.246(7) and 1.254(7) Å), while the N–C distances are inequivalent (1.424(7) and 1.374(6) Å). Overall, these metrical parameters suggest the presence of a localized π-bond between N3 and C31 and localization of the unpaired electron at C30, as drawn for **2** in Scheme 2. The sum of interatomic angles around N3 (360.0°) is also consistent with this hypothesis.

The X-band solution-phase EPR spectrum of complex **2**, recorded in toluene at room temperature, displays a narrow isotropic peak at g = 2.0010 indicative of an S = 1/2 organic radical (Figure 3; see also Figure S5).[69] Upon cooling to 110 K, the EPR spectrum of **2** remains centered at the same g value, but broadens somewhat (Figure S6). To better understand these spectra, the electronic structure of **2** was investigated by density functional theory (DFT) calculations using the ORCA software package.[70,71] For computational efficiency and simplicity, the β-diketiminate Ar groups were replaced by Me groups. This truncated structure is denoted **2′**. The [K(2.2.2-cryptand)]$^+$ moiety was also omitted. Its optimized geometry, **2′-opt**, differs only slightly from the experimental structure (Figures S14 and S15; Cartesian coordinates are given in Table S4). Nevertheless, the optimized structure maintained the *O*,*O*-κ^2 chelate interaction.

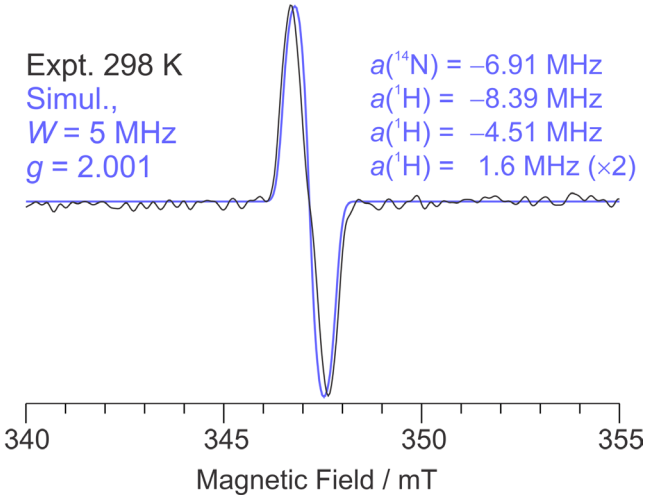


Figure 3. Room temperature X-band EPR spectrum (black trace) of **2** (4.9 mM in toluene; 9.72515 GHz; field modulation amplitude 4.0 G) with simulation (lavender trace). The simulation parameters are based on DFT calculations that provided isotropic hyperfine coupling constants for the ^{14}N and ^{1}H nuclei in **2′-opt** (see Table S3; only the largest magnitude couplings are included). It is possible to simulate the experimental spectrum absent any hyperfine coupling, but with a broader linewidth (13 MHz, Gaussian, hwhm).

We also calculated the EPR parameters for **2′** and **2′-opt**; specifically, the **g** tensor and hyperfine coupling tensors for ^{14}N and ^{1}H (Table S3). The values for **2′** and **2′-opt** are essentially identical, and only those of **2′-opt** will be discussed in detail. For comparison, these parameters were calculated also for PINO$^\bullet$ (see SI for complete computational details). In all cases, the calculated **g** tensors were very close to the free electron value with anisotropy in the range of that observed experimentally. More importantly, the nitroxyl ^{14}N hyperfine coupling calculated for **2′-opt** is reduced from that for PINO$^\bullet$, while coupling to the four H atoms of the aryl ring is increased relative to that for PINO$^\bullet$.[72] As a consequence of the reduced $|A(^{14}N)|$ value and increased $|A(^1H)|$ values, the EPR signal of **2** appears as a singlet, rather than the resolved triplet of PINO$^\bullet$ and other related nitroxyl radicals.[2] The nature of the delocalization within the phthalimide fragment can also be seen by inspecting the relevant molecular orbital (91α in **2′-opt**), which is shown in Figure 4.

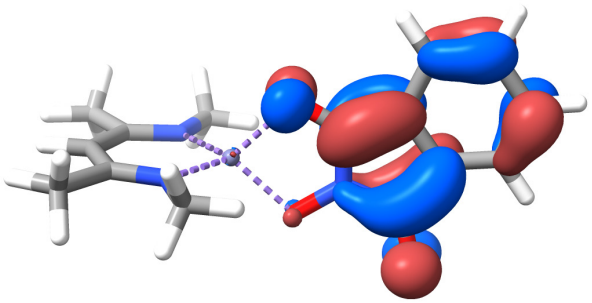


Figure 4. Isosurface (±0.04 au) of the SOMO (91α) in **2′-opt**.

Intriguingly, the hyperfine coupling to ^{67}Zn is calculated to be non-zero (ranging from 1.5 – 2.0 MHz, depending on model). This value is too small to generate satellite peaks, in contrast to the spectrum observed for the closely-related Mg complex, [^{Me}LMg(OCPh$_2$)(DMAP)].[73] Nonetheless, this prediction inspired us to use the results of Rieger to estimate what such a species would yield in terms of spin population on Zn (Table S6).[74,75] In this regard, our extrapolation of Rieger's method corresponds to <0.1% of a spin, demonstrating that **2** is definitively a Zn(II) coordination complex.

In summary, we have structurally characterized the first example of a *N*-oxy-phthalimide complex featuring radical character within its phthalimide ligand, definitively establishing the redox activity of this ligand. Our EPR spectroscopic studies reveal a $S = 1/2$ delocalized organic radical with a smaller $|A(^{14}N)|$ hyperfine coupling relative to typical nitroxyl radicals. These data are somewhat inconsistent with the solid-state metrical parameters of the reduced *N*-oxy-phthalimide fragment, which suggest that the radical is localized on a carbonyl group. Nonetheless, these structural and spectroscopic insights should facilitate further development of *N*-(acyloxy)phthalimide decarboxylation in organic synthesis. This work also expands the range of structurally-characterized redox-active ligands.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, crystallographic details, and spectral data for **1** and **2**, DFT procedures and output tables, along with further discussion of hyperfine coupling (PDF). This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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SYNOPSIS TOC: Characterization of [K(2.2.2-cryptand)][^{Me}LZn(OPth)] (^{Me}L = {(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(Me)}$_2$CH) via X-ray crystallography and EPR spectroscopy reveals the presence of an S = 1/2 radical on the phthalimide ligand.