# **Inorganic Chemistry**

# Anion Effects in Oxidative Aliphatic Carbon-Carbon Bond Cleavage **Reactions of Cu(II) Chlorodiketonate Complexes**

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**S** Supporting Information

ABSTRACT: Aliphatic oxidative carbon-carbon bond cleavage reactions involving Cu(II) catalysts and O<sub>2</sub> as the terminal oxidant are of significant current interest. However, little is currently known regarding how the nature of the Cu(II) catalyst, including the anions present, influence the reaction with O2. In previous work, we found that exposure of the Cu(II) chlorodiketonate complex [(6-Ph<sub>2</sub>TPA)Cu(PhC-(O)CClC(O)Ph) ClO<sub>4</sub> (1) to O<sub>2</sub> results in oxidative aliphatic carbon-carbon bond cleavage within the diketonate unit, leading to the formation of benzoic acid, benzoic anhydride, benzil, and 1,3-diphenylpropanedione as organic products. Kinetic studies of this reaction revealed a slow induction phase followed by a rapid decay of the absorption features of 1. Notably, the induction phase is not present when the reaction is performed in the presence of a catalytic amount of chloride anion. In the studies presented herein, a combination of spectroscopic (UV-vis, EPR) and density



functional theory (DFT) methods have been used to examine the chloride and benzoate ion binding properties of 1 under anaerobic conditions. These studies provide evidence that each anion coordinates in an axial position of the Cu(II) center. DFT studies reveal that the presence of the anion in the Cu(II) coordination sphere decreases the barrier for O<sub>2</sub> activation and the formation of a Cu(II)-peroxo species. Notably, the chloride anion more effectively lowers the barrier associated with O-O bond cleavage. Thus, the nature of the anion plays an important role in determining the rate of reaction of the diketonate complex with  $O_2$ . The same type of anion effects were observed in the  $O_2$  reactivity of the simple Cu(II)-bipyridine complex  $[(bpy)Cu(PhC(O)C(Cl)C(O)Ph)ClO_4]$  (3).

# INTRODUCTION

Oxidative aliphatic carbon-carbon (C-C) bond cleavage reactions catalyzed by first-row transition metal salts that involve O2 as the terminal oxidant are of significant current interest for the preparation of bulk and fine chemicals.<sup>1</sup> These reactions have the potential to offer more economically feasible, environmentally friendly, and sustainable processes than those employing expensive precious-metal catalysts and harsh oxidants. However, essential to optimizing the use of first-row metal catalysts with O2 for oxidative catalysis is an understanding of the factors that influence O2 activation and O-O bond cleavage in such systems. The tremendous advances in recent years in understanding the interplay of metal ions and  $O_2$  in biological oxidative processes offer considerable insight into possible mechanistic pathways. However, as the first-row metal salts and supporting ligands that are employed in synthetic organic oxidative processes typically lack the sophistication of an enzyme active site, it is important to define mechanistic pathways in relatively simple molecular systems that can be further modified to move toward understanding catalytic conditions.

Of particular current interest are copper/O2-catalyzed reactions that result in aliphatic C-C bond cleavage adjacent to a ketone carbonyl moiety.<sup>2</sup> Optimized conditions reported for these reactions can involve either Cu(I) (e.g., CuX,  $X = CI^{-}$ , Br<sup>-</sup>, I<sup>-</sup>) or Cu(II) salts (e.g., CuCl<sub>2</sub> or Cu(OAc)<sub>2</sub>), with analogues containing different anions frequently giving significantly different product yields despite the same starting copper oxidation state. Jiao recently reported Cu/O2-catalyzed aliphatic C-C bond cleavage reactions involving 1,3-diketone substrates that result in the formation of either  $\alpha$ -keto ester or 1,2-diketone products (Scheme 1).<sup>3</sup> Notably, the highest product yields were obtained using either CuBr or CuBr<sub>2</sub> as the copper source. Screening studies of these reactions using other copper salts (CuX,  $X = Cl^{-}$ ,  $I^{-}$ , OAc<sup>-</sup>) gave only trace amounts of the 1,2-diketone product. Other previously reported examples of Cu/O2-mediated oxidative aliphatic C-C bond cleavage reactions involving  $\beta$ -diketone-type enolate substrates were optimized using other copper/anion combina-

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Scheme 1. Cu/O<sub>2</sub>-Mediated Aliphatic C–C Bond Cleavage Reactions Involving Enolate-Type Substrates



tions, including  $Cu(NO_3)_2$  or  $Cu(ClO_4)_2$  (Scheme 1).<sup>4</sup> Overall, little is currently known regarding how the anions present in  $Cu/O_2$ -mediated C–C bond cleavage processes affect the reaction pathway.

Halide effects have been investigated for a variety of transition-metal-catalyzed processes.<sup>5</sup> However, only recently have studies begun to emerge regarding halide effects on copper-mediated redox processes, including those involving  $O_2$  activation and Cu(II)/1,3-diketone redox reactivity.<sup>6</sup> These initial investigations have focused primarily on the use of X-ray absorption spectroscopy and electron paramagnetic resonance (EPR) spectroscopy to identify stable Cu(I) and Cu(II) species in the reactivity of a particular copper oxidation state in the  $O_2$  activation process is currently undefined, it could be of significance toward understanding the differing reactivities exhibited in the aliphatic C–C bond cleavage reactions described above.

We recently reported that exposure of the Cu(II) chlorodiketonate complex 1 (Scheme 2) to  $O_2$  results in oxidative C–C bond cleavage within the diketonate unit to give benzoic acid, benzoic anhydride, benzil, diphenylpropanetrione, the Cu(II) chloride complex 2, and a CO<sub>2</sub>/CO mixture (0.80:0.05 equiv).<sup>7</sup> The Cu(II) center is needed for  $O_2$ 

#### Scheme 2. Reaction of 1 with $O_2$



activation in this system, as the chlorodiketonate anion is unreactive with O2. <sup>18</sup>O-labeling studies revealed incorporation of at least one <sup>18</sup>O-labeled oxygen atom in 60% of the benzoic acid product. A <sup>16</sup>O<sub>2</sub>/H<sub>2</sub><sup>18</sup>O experiment showed incorporation of labeled oxygen into 30% of the benzoic acid product. Under dry conditions, benzoic anhydride is formed and quantitative <sup>18</sup>O incorporation in the diphenylpropanetrione intermediate is found. Overall, this combined information points toward a reaction pathway wherein aliphatic C-C bond cleavage results from the reaction of a diphenylpropanetrione intermediate with HOCl or H<sub>2</sub>O<sub>2</sub> generated in the reaction mixture. Notably, an independently performed reaction between [(6-Ph<sub>2</sub>TPA)Cu- $(CH_3CN)$  (ClO<sub>4</sub>)<sub>2</sub>, diphenylpropanetrione, and NaOCl gave the same product mixture (including the same gas ratio) as the reaction of 1 with O2, thus suggesting a trione/hypochlorite pathway for C-C bond cleavage.

Kinetic studies of the reaction of 1 with  $O_2$  showed a slow induction phase followed by a rapid first-order decay process (Figure 1). Notably, the induction phase was removed in the



Figure 1. Plots of absorbance (monitoring at 362 nm) vs time for the reactions of 1 with  $O_2$  in the absence and presence of added  $Me_4NCl$  (0.05 equiv).

presence of a catalytic amount of chloride ion. Preliminary computational studies provided evidence that chloride coordination to the Cu(II) center of 1 removed the induction phase by lowering the barrier for the rate-determining  $O_2$  activation step.<sup>7</sup>

In the results reported herein, further spectroscopic and computational studies of this system provide insight into the copper coordination environment of 1 in the presence of chloride ion and demonstrate the influence of chloride coordination on  $O_2$  activation and O-O bond cleavage. Notably, we have found that the nature of the anion is critical for achieving maximum rate enhancement. Specifically, studies of 1 in the presence of added benzoate indicate that coordination of this anion to the Cu(II) center extends the induction phase by altering the barrier associated with the O-O bond cleavage step. Overall, these studies provide unprecedented new insight into anion effects in Cu(II)/ $O_2$ -mediated aliphatic C–C bond cleavage.

#### RESULTS

Anaerobic Chloride Ion Binding Studies. Absorption Spectra. The interaction of 1 with added chloride ion (from Bu<sub>4</sub>NCl) was evaluated in CH<sub>3</sub>CN under anaerobic conditions

using UV–vis spectrophotometry at 25 °C. As was previously reported, acetonitrile solutions of 1 in the presence of trace chloride ion exhibit enhanced  $O_2$  reactivity. Therefore, a series of measurements were performed on individually prepared samples containing 1 and increasing amounts of chloride ion. As shown in Figure 2, addition of chloride ion to a CH<sub>3</sub>CN



**Figure 2.** Absorption spectral changes in the (a)  $\pi \rightarrow \pi^*$  and (b) d–d regions observed upon addition of various amounts of chloride ion to a CH<sub>3</sub>CN solution of 1 under anaerobic conditions.

solution of 1 results in changes in both the chlorodiketonate  $\pi$  $\rightarrow \pi^*$  absorption band and the Cu(II) d–d transition region of 1. Both show consistent absorbance values after the addition of ~10 equiv of chloride ion. The  $\pi \rightarrow \pi^*$  band increases in intensity, whereas the Cu(II) d-d feature shifts to lower energy and increases in intensity. The changes in the d-d region proceed with a possible isosbestic point at ~630 nm. To evaluate whether the d-d band changes are the result of a twostate system wherein 1 and a possible chloride adduct are the only absorbing species present, Rose-Drago plots were constructed using wavelengths in both ranges (Figure S1).<sup>8</sup> For a two-state system, plotting the change in absorbance at a specific wavelength for two different concentrations (i and k)versus the change in absorbance at a different wavelength for concentrations j and k (i.e.,  $(A_{1i} - A_{1k})$  versus  $(A_{2i} - A_{2k})$ ) will yield a plot with two lines of different slopes passing through the origin.<sup>8</sup> As shown in Figure S1, this is the case for both the  $\pi \rightarrow \pi^*$  and d-d transition data for 1 in the presence of chloride ion, suggesting the presence of the equilibrium shown in eq 1:

$$[(6-Ph_2TPA)Cu(PhC(O)C(Cl)C(O)Ph)]^{+} + Cl^{-}$$

$$\downarrow [(6-Ph_2TPA)Cu(PhC(O)C(Cl)C(O)Ph)(Cl)]$$

$$I_{Cl} \qquad (1)$$

Modeling of the 500–800 nm data using HypSpec2014<sup>9</sup> was performed for the equilibrium shown in eq 1. The spectral features obtained (Figure S2) are in good agreement with the experimental results, and the equilibrium constant determined (log K = 1.84(3)) is similar to that found for other Cu(II) complexes binding a second anion.<sup>10</sup>

*EPR Spectra.* The d-d absorption features of 1 in the presence of excess chloride ion suggest that a distorted square-pyramidal geometry similar to that found in 1 is maintained for  $1_{CL}$ .<sup>11</sup> This is further supported by the EPR features of 1 in the presence of excess chloride ion (Figure 3), which indicate the formation of a new species that retains the  $d_{x^2-y^2}$  ground state  $(g_{\parallel} > g_{\perp})$ .<sup>11</sup>



**Figure 3.** EPR features of 1 and 1 + 5 equiv of Cl<sup>-</sup> at 20 K. For 1,  $g_{\parallel} = 2.23$ ,  $g_{\perp} = 2.03$ , and  $A_{\parallel}(^{63,65}\text{Cu}) = 420$  MHz.

Computational Studies. Chloride Coordination. Density functional theory (DFT) calculations were performed to gain further insight into (a) the structural and electronic features associated with chloride coordination to the Cu(II) center of 1 and (b) the reaction pathway for  $O_2$  activation and aliphatic C-C bond cleavage in 1 and 1<sub>Cl</sub>. The DFT geometry-optimized structures of 1 and 1<sub>Cl</sub> are shown in Figure 4. A detailed comparison of the bond distances involving the Cu(II) center in the X-ray structure of 1 versus the DFT geometry-optimized structure of this compound is provided in Table S1. Overall, the geometry-optimized structure of 1 is very similar to that identified by X-ray crystallography, although the axial Cu-N<sub>PhPv</sub> distances are more equal (DFT: 2.437 and 2.501 Å; X-ray crystallography: 2.3394(18) and 3.09 Å; avg. 2.715 Å). Considering the sum (2.39 Å) of the van der Waals radius of nitrogen (1.6 Å) and the ionic radius of five-coordinate Cu(II) (0.79 Å), the interactions with the phenyl-appended pyridyl donors in 1 via X-ray crystallography can be described as consisting of one strong and one weak interaction, whereas the DFT results are consistent with two weak interactions.<sup>12</sup>

The geometry-optimized structure of  $\mathbf{1}_{CI}$  contains a Cu(II) center that is distorted square-pyramidal ( $\tau = 0.37$ ;<sup>13</sup> Table S1) with complete displacement of one phenyl-appended pyridyl donor. The second N<sub>PhPy</sub> group is positioned trans to the chloride ligand and, while being oriented toward the Cu(II) center, is positioned at a distance beyond that possible for bonding (3.008 Å). This geometry is consistent with the UV–



Figure 4. DFT geometry-optimized structures of 1 and 1<sub>Cl</sub>. Selected bond distances are given in Table S1.

Scheme 3. Comparison of the Lowest-Energy  $O_2$  Activation and O-O/C-Cl Bond Cleavage Pathways for 1 and  $1_{Cl}$ 



#### reaction coordinate

Figure 5. Plots of calculated enthalpy vs reaction coordinate for steps in the reactions of 1 and  $1_{Cl}$  with  $O_2$ .

vis and EPR spectroscopic features described above for the species formed upon addition of excess chloride ion to 1. The

Cu–Cl distance in  $\mathbf{1}_{Cl}$  (2.448 Å) is consistent with its position as an axial ligand.<sup>14</sup>





 $O_2$  Activation. Several approaches for  $O_2$  activation were computationally investigated for 1 and  $1_{Cl}$ . These included (1) electronic excitation to a Cu(I)-enolate radical charge transfer state followed by reaction with  $O_2$  and (2) direct attack of  $O_2$ on the central carbon of the enolate ligand. Time-dependent DFT (TD-DFT) with the CAM-B3LYP functional was used to optimize the lowest-lying ligand-to-metal charge transfer (LMCT) state as well as the ground state of 1 (Figure S3 and Table S2). The computed adiabatic excitation energy to this enolate-to-Cu charge transfer state is 40.0 kcal/mol, which argues against the possibility that the Cu(II) ion oxidizes the diketonate to a radical. All attempts to bind dioxygen exclusively to the copper center or the chlorodiketonate ligand led to species with unacceptably high energies. However, the peroxo intermediate with an O–O bridge between Cu(II) and the chloro-substituted carbon of the diketone (1-P and  $1-P_{CI}$  in Scheme 3) is predicted to be formed in an exothermic process (Figure 5). The transition state structure TS1 for trapping of O<sub>2</sub> by 1 (Figure S4 and Table S3) exhibits dioxygen coordination to copper at a coordination site made available by dissociation of one of the oxygen atoms of the chlorodiketonate ligand. From spin populations for TS1 it follows that at this point the organic substrate is already oneelectron-oxidized by  $O_{2}$ , with a Cu(II)-bound superoxide anion. Since the unpaired electrons on these two entities have antiparallel spins, they quench, forming the peroxo intermediate 1-P (Figure S5 and Table S4). The computed barrier connected with TS1 is substantial (25.9 kcal/mol), which indicates a slow process. The geometry of TS1 was slightly perturbed and subsequently optimized to a species that can be characterized as Cu(II)-superoxide/diketonate radical complex. With the basis set used for optimization (BS1), this species is only marginally more stable than TS1, but when the energy is corrected for basis set, solvent, and thermal effects and spin projection, this species is predicted to be less stable than TS1. Hence it was concluded that such a species is not a stable minimum. When a chloride is bound to the Cu(II) center, the process of O2 trapping proceeds in a very similar way (TS1<sub>Cl</sub>; Figure S4 and Table S3), yet the enthalpy barrier connected with  $TS1_{Cl}$  to form  $1-P_{Cl}$  (Figure 5) is much smaller, i.e., 16.9 kcal/mol. Variable-temperature kinetic studies of the reaction of 1 with  $O_2$  in the presence of 0.05 equiv of  $Bu_4NCl$ 

gave an enthalpic barrier of 10(1) kcal/mol (Figure S6). The relative congruence of the enthalpy values between experiment and theory provides a benchmark for the calculations.

The Cu–Cl distance in TS1<sub>Cl</sub> and 1-P<sub>Cl</sub> (~2.35 Å) is consistent with the chloride being shifted into the basal plane of these distorted square-pyramidal structures ( $\tau = 0.03$  and 0.32, respectively).<sup>13</sup> In the 1-P<sub>Cl</sub> structure, the only interaction with the chlorodiketonate unit is via the peroxo bridge, whereas in 1-P a carbonyl moiety remains coordinated to the Cu(II) center.

O-O and C-Cl Bond Cleavage. Participation of the diphenylpropanetrione intermediate in the reaction suggests that the progress of the reaction beyond the peroxo intermediates (1-P and 1-P<sub>Cl</sub>) requires cleavage of the O-O bond and release of the halogen from the central carbon. Cleavage of the O-O bond can be realized in either a heterolytic or homolytic process. The former requires a good overlap between the O–O  $\sigma^*$  orbital and an electron-pair donor orbital, whereas the latter would proceed with a straightforward O–O bond elongation leaving unpaired electrons of opposite spin on the two oxygen atoms. For the studied systems (1-P and 1- $P_{Cl}$ ), the halogen provides an electron pair interacting with the O–O  $\sigma^*$  orbital during O–O cleavage. This is a rather intricate process for species 1-P, as before the transition structure TS2 is reached the proximal oxygen atom of the O-O bridge approaches the central carbon and expels the chloride anion in an S<sub>N</sub>2-like process. The chloride ion migrates toward the distal oxygen and elicits heterolytic cleavage of the O-O bond, yielding ClO<sup>-</sup> bound to the triketone species (1-T; Figure S7 and Table S6). Thus, in a single reaction step two bonds are formed (C-O and Cl-O) and two are cleaved (C-Cl and O-O). The computed barrier for this process amounts to 24.7 kcal/mol, which is comparable to the barrier for  $O_2$  trapping. For  $\mathbf{1}_{Cl}$  the presence of the chloride ligand in the first coordination sphere makes a big difference since this ligand can easily provide the electron pair required for O-O bond heterolysis. In TS2<sub>Cl</sub> the chloride ligand attacks the proximal oxygen atom from the O–O group, which elicits O-O bond cleavage and expulsion of the chloride from the central carbon. Importantly, the computed barrier for  $TS2_{Cl}$  (11.6 kcal/mol) is markedly lower than that for TS2 (24.7 kcal/mol). Atomic spin populations computed for TS2 and TS2<sub>Cl</sub> show no spin on the chloride expelled from the Scheme 5. Reaction Pathway Involving Triketone and Hypochlorite Intermediates Leading to Aliphatic C-C Bond Cleavage



Scheme 6. Synthetic Route for the Preparation of 3



Figure 6. (left) Representation of the X-ray structure of 3. Hydrogen atoms have been omitted for clarity. (center) Comparison of the absorption spectral features of 1 and 3 in CH<sub>3</sub>CN. (right) EPR spectrum of 3 in CH<sub>3</sub>CN at 4.5 K. For 3,  $g_{\parallel} = 2.16$ ,  $g_{\perp} = 1.97$ , and  $A_s = 561$  MHz.

central carbon, which confirms that this is a heterolytic processes.

With respect to the homolytic mechanism, we were able to optimize a relevant transition state for the 1-P<sub>CI</sub> system (TS2<sub>Cl homo</sub>; Figure S8 and Table S7). The barrier for O-O bond homolysis is 5.4 kcal/mol higher than for the heterolytic process proceeding with oxidation of the first-shell Cl ligand (TS2<sub>Cl homo</sub> vs TS2<sub>Cl</sub>; Figure 5). For 1-P, instead of an optimized TS for the homolytic path, a TS for heterolytic O–O bond cleavage (TS2<sub>ph</sub>; Figure S9 and Table S8) proceeding with oxidation of one of the phenyl rings of the chelate  $(T_{Ph};$ Figure S10 and Table S9) was obtained. A similar pathway was identified for 1-P<sub>Cl</sub> (TS2<sub>Cl Ph</sub> and T<sub>Cl Ph</sub>; Figures S11 and S12 and Tables S10 and S11, respectively). For 1-P this result indicates that the homolytic process most likely involves a barrier higher than that associated with TS2<sub>Ph</sub>. Notably, the reaction channel for 1-P involving arene oxidation  $(TS2_{Ph})$  has an enthalpy that is 4.9 kcal/mol lower than TS2 (Figure 5).

This suggests that the initial lag phase seen in the reaction of 1 with  $O_2$  may involve arene oxidation with release of chloride anion. However, as <5% of the reaction occurs prior to the onset of the more rapid decay associated with the chloride-promoted pathway, we have been unable to spectroscopically identify any oxidized ligand. Arene oxidation is not expected for the 1-P<sub>Cl</sub> system (Scheme 4), as oxidation of the phenyl ring involves a barrier that is 11.5 kcal/mol higher than for the O– O cleavage proceeding with oxidation of the Cl ligand (TS2<sub>Cl Ph</sub> vs TS2<sub>Cl</sub>; Figure 5).

Aliphatic C–C Bond Cleavage. As this reaction is suggested to happen after the formation of the diphenylpropanetrione/  $CIO^-$  intermediate (1-T or 1-T<sub>CI</sub>; Figure S7 and Table S6) and proceeds with no direct involvement of the Cu(II) ion, it is expected that there will be similar barriers irrespective of the presence or absence of chloride anion in the copper coordination sphere. Accordingly, these reaction steps were studied only for the parent system. The hypochlorous anion bound to the central carbon of the triketone intermediate can easily exert its oxidative power by incorporating an oxygen atom into the adjacent C-C bond. Insertion into the noncoordinated end of the triketone (TS3) proceeds with no barrier and leads to species M (Scheme 5 and Figure S13) featuring a mixed (ketoacid/acid) anhydride. The  $T \rightarrow M$  step is highly exothermic, i.e., -58.6 kcal/mol. The mixed ketoacid/ acid anhydride moiety of intermediate M has one more C-C bond that might be prone to oxidation. Thus, we tested a mechanism whereby the chloride anion in the second coordination sphere is replaced by ClO<sup>-</sup> that might be released from the T intermediate. In M-ClO (Figure S13), the ClO<sup>-</sup> is bound to the central carbon, and in a reaction step via TS4 it inserts an oxygen atom into the C-C bond of the ketoacid fragment of the anhydride. The calculated barrier connected with this step is low and amounts to 8.6 kcal/mol, whereas the exothermicity is substantial, i.e., -61.2 kcal/mol. In the resulting product complex M2 (Figure S13), a mixed anhydride of carbonic and benzoic acid is expected to yield CO<sub>2</sub>, benzoic acid, and benzoyl chloride. The overall reaction energy profiles for the reactions of 1 and  $1_{CI}$  with  $O_2$  are given in Figure 5.

Evaluation of the Supporting Ligand. The DFT geometry-optimized structures of 1 and 1<sub>Cl</sub> and intermediates in the reaction pathways reveal that the phenyl-appended pyridyl donors of the 6-Ph<sub>2</sub>TPA chelate are at best only weak ligands to the Cu(II) center. To evaluate whether these donors influence the reaction pathway, we prepared, characterized, and evaluated the  $O_2$  reactivity of [(bpy)Cu(PhC(O)C(Cl)C(O)-Ph)  $ClO_4$  (3) (Scheme 6). As shown in Figure 6(left) and Tables 1 and 2, the cationic portion of this compound is nearly perfectly square-pyramidal ( $\tau = 0.04$ ).<sup>13</sup> When dissolved in CH<sub>3</sub>CN, 3 exhibits UV-vis and EPR features (Figure 6 (center and right)) consistent with retention of the square-pyramidal geometry and similar to those of 1. Exposure of CH<sub>3</sub>CN solutions of 3 to  $O_2$  at room temperature gives organic products (benzoic acid, benzil) and a gas mixture ratio  $(CO_2:CO = 0.70:0.30)$  similar to that observed for 1. However, the primary Cu(II) product identified by mass spectrometry is  $[Cu(bpy)_2(ClO_4)]^+$  (Figure S14), indicating that ligand exchange has occurred. The kinetic features of the reaction of 3 with  $O_2$  are also similar to those observed for 1, with an induction phase followed by a rapid first-order decay process (Figure S15). The pseudo-first-order rate constant with respect to  $O_2$  for the fast portion  $(3.25(3) \times 10^{-3} \text{ s}^{-1})$  is slightly larger than that found for 1  $(2.2(4) \times 10^{-3} \text{ s}^{-1})$ . The induction phase can also be eliminated by the addition of a catalytic amount of chloride anion. Specifically, in the presence of 0.05 equiv of chloride ion, the induction phase is removed while the rate constant for the rapid decay portion remains similar  $(3.2(1) \times$  $10^{-3} \text{ s}^{-1}$ 

The spectroscopic changes under anaerobic conditions are consistent with coordination of a single chloride ion to the Cu(II) center of **3** in a two-state system (Figure S16). The binding constant for coordination of one chloride ion to **3** (log K = 4.1(7)) is higher than that observed for **1**, which is likely due to the lower coordination number of the Cu(II) center in **3**. Overall, the properties of **3** indicate that a simple bidentate chelate ligand is sufficient to support the Cu(II)/O<sub>2</sub> chemistry and halide effects seen previously in the 6-Ph<sub>2</sub>TPA-ligated system.

**Does Benzoate Anion Produce a Similar Effect?** The observed rate enhancement for the reaction of 1 and 3 with  $O_2$  in the presence of chloride ion is novel. To examine whether

Table 1. Summary of X-ray Data Collection and Refinement for  $3 \cdot CH_3CN$  and 4

	3-CH <sub>3</sub> CN	4	
empirical formula	C <sub>25</sub> H <sub>18</sub> CuN <sub>2</sub> Cl <sub>2</sub> O <sub>6</sub> ·CH <sub>3</sub> CN	C37H31CuN4ClO6	
formula weight	617.91	726.65	
crystal system	monoclinic	monoclinic	
space group	$P2_1/n$	$P2_{1}/c$	
a (Å)	9.0564(3)	11.0622(3)	
b (Å)	20.6815(8)	24.4722(6)	
c (Å)	14.3598(5)	12.2273(3)	
$\alpha$ (deg)	90	90	
$\beta$ (deg)	106.036(2)	100.6170(10)	
γ (deg)	90	90	
$V(Å^3)$	2584.93(16)	3253.46(14)	
Ζ	4	4	
calcd density (Mg m <sup>-3</sup> )	1.588	1.483	
T (K)	150(1)	150(1)	
crystal size (mm <sup>3</sup> )	$0.39 \times 0.17 \times 0.17$	$0.43 \times 0.31 \times 0.11$	
diffractometer <sup>a</sup>	Nonius Kappa CCD	Nonius Kappa CCD	
abs. coeff. (mm <sup>-1</sup> )	1.101	0.809	
max $2\theta$ (deg)	60.06	55.8342	
reflections collected	52276	89920	
indep. reflections	7570	7757	
variable parameters	353	442	
$R_1/wR_2^b$	0.0342/0.0817	0.0284/0.0670	
goodness of fit $(F^2)$	1.033	1.030	
largest diff. (e Å <sup>-3</sup> )	0.414; -0.398	0.337; -0.340	
<sup><i>a</i></sup> Radiation used: Mo K $\alpha$ ( $\lambda = 0.71073$ Å). <sup><i>b</i></sup> $R_1 = \sum   F_0  -  F_c   / \sum  F_0 $ ;			

"Radiation used: Mo K $\alpha$  ( $\lambda = 0.710/3$  A). " $R_1 = \sum ||F_o| - |F_c|/\sum |F_o|$ ;  $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2]/\sum [(F_o^2)^2]\}^{1/2}$ , where  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ .

Table 2. Selected Bond Distances (Å) and Angles (deg) for  $3 \cdot CH_3CN$  and 4

	3-CH <sub>3</sub> CN	4
Cu(1) - O(1)	1.9008(11)	1.8982(10)
Cu(1) - O(2)	1.9112(11)	
Cu(1)-N(1)	1.9878(14)	2.0464(12)
Cu(1)-N(2)	1.9918(4)	2.0176(12)
Cu(1) - O(3)	2.3716(13)	
Cu(1) - N(3)		2.2006(12)
Cu(1)-N(4)		2.1009(12)
N(1)-Cu(1)-O(1)	171.68(5)	97.58(5)
O(1)-Cu(1)-O(2)	91.19(5)	
O(2)-Cu(1)-N(1)	93.46(5)	
O(1)-Cu(1)-N(2)	92.63(5)	175.20(5)
N(2)-Cu(1)-O(2)	170.07(5)	
N(1)-Cu(1)-N(2)	81.71(6)	81.85(5)
O(1) - Cu(1) - O(3)	91.21(5)	
O(2) - Cu(1) - O(3)	93.57(5)	
N(1)-Cu(1)-O(3)	95.39(5)	
N(2)-Cu(1)-O(3)	95.51(3)	
O(1)-Cu(1)-N(4)		98.10(5)
N(2)-Cu(1)-N(4)		79.18(5)
N(1)-Cu(1)-N(4)		135.27(5)
O(1)-Cu(1)-N(3)		105.17(5)
N(2)-Cu(1)-N(3)		79.48(5)
N(1)-Cu(1)-N(3)		108.39(5)
N(3)-Cu(1)-N(4)		107.39(5)

other anions show a similar effect, we investigated whether benzoate, another anion generated in the reaction of 1 and 3 with  $O_{22}$  produces similar reactivity. We previously crystallized the Cu(II) chloride complex 2 (Scheme 2) from the crude mixture from the reaction of 1 with  $O_2$  and reported this compound as the only Cu(II) product. Congruence of the EPR features of the product mixture with an independently generated sample of 2 further supported this proposal. Subsequent ESI-MS analysis of the product mixture (Figure S17) indicated that the Cu(II) benzoate complex [(6-Ph<sub>2</sub>TPA)Cu(OC(O)Ph)]ClO<sub>4</sub> (4) is also a product in the reaction mixture. To further characterize this compound, 4 was independently synthesized and characterized. Similar to 2, the Cu(II) center in 4 (Figure 7) exhibits a distorted trigonal-



**Figure 7.** Representation of the cationic portion of the X-ray structure of **4**. Hydrogen atoms have been omitted for clarity.

bipyramidal geometry (2:  $\tau = 0.61$ ; 4:  $\tau = 0.67$ ).<sup>13</sup> Changes in the d-d band region for the reaction of 1 with O<sub>2</sub> (Figure 8) suggest that a mixture of 2 and 4 is present in the product mixture. The EPR spectrum of the product mixture is also consistent with the presence of 4 (Figure S18).



**Figure 8.** Comparison of the d-d band regions of the absorption spectra of 1,  $1 + O_2$ , and independently generated 2 and 4.

Notably, the addition of 0.05 equiv of  $Bu_4NOC(O)Ph$  to a  $CH_3CN$  solution of 1 under excess  $O_2$  does not result in the loss of the induction phase (Figure 9 inset) and increasing the



**Figure 9.** Plots of absorption vs time for reactions of **1** with  $O_2$  in the presence of varying amounts of  $Bu_4NOC(O)Ph$  at 25 °C. Inset: expanded view of the plots for the reactions involving the addition of 0 equiv (black), 0.05 equiv (blue), 0.25 equiv (red), and 0.50 equiv (green) of  $Bu_4NOC(O)Ph$ .

amount of benzoate present up to ~0.25 equiv produces no significant change in the kinetics of the reaction of 1 with O<sub>2</sub>. However, further increasing the amount of added benzoate to 0.50–1.0 equiv produces longer induction periods (Figure 9) prior to a rapid first-order decay process. The rate constants for the rapid decay portion increase only slightly with added benzoate (from  $2.0 \times 10^{-3}$  to  $3.0 \times 10^{-3}$  s<sup>-1</sup>) versus a more dramatic increase in the presence of added chloride ion (Figure S19). Thus, increasing the amount of benzoate ion lengthens the induction phase and produces no significant rate enhancement for the rapid first-order decay process.

Addition of benzoate (from Bu<sub>4</sub>NOC(O)Ph) to CH<sub>3</sub>CN solutions of 1 at 25 °C under anaerobic conditions produces spectroscopic changes in the chlorodiketonate  $\pi \rightarrow \pi^*$  band. As shown in Figure 10, this absorption band loses intensity and is blue-shifted from 363 to 352 nm. The data generated using independently prepared samples suggest the presence of multiple isosbestic points in the region of 300–500 nm. Fitting of the data using the Rose–Drago method (Figure S20) indicated a two-state system described by eq 2:

$$[(6-Ph_2TPA)Cu(PhC(O)C(Cl)C(O)Ph)]^+ + {}^{-}OC(O)Ph$$

$$\stackrel{I}{\approx} [(6-Ph_2TPA)Cu(PhC(O)C(Cl)C(O)Ph)(OC(O)Ph)]$$

$$\stackrel{I_b}{\qquad} (2)$$

Modeling of these data using HypSpec2014 (Figure S21) identified two isosbestic points at 347 and 380 nm and an



Figure 10. Spectral changes observed upon addition of  $Bu_4NOC(O)$ -Ph to a  $CH_3CN$  solution of 1 at 25 °C under anaerobic conditions.

estimated log K value of 2.81(2). We note that benzoate ion coordination could not be examined at the high concentrations necessary to examine the d-d transition region for 1 because of displacement of the 6-Ph<sub>2</sub>TPA chelate ligand and the formation of an insoluble solid particulate of  $Cu(OC(O)Ph)_2$  (identified by IR spectroscopy).

EPR spectral data for  $\mathbf{1}_b$  were collected via the addition of 5 equiv of  $Bu_4NOC(O)Ph$  to a  $CH_3CN$  solution of 1 (Figure S22). Similar to the case of  $\mathbf{1}_{Cb}$  the data suggest retention of the distorted square-pyramidal geometry in a benzoate-coordinated structure.

**Computational Studies.** The DFT geometry-optimized structure of  $1_b$  is shown in Figure 11. Similar to the case of  $1_{CP}$ 



Figure 11. DFT geometry-optimized structure of  $1_b$ . Selected bond distances are given in Table S12.

the benzoate adduct exhibits a distorted square-pyramidal geometry ( $\tau = 0.19$ ;<sup>13</sup> Table S12) with the benzoate ligand in the axial position, one phenyl-appended pyridyl donor completely displaced from the Cu(II) center, and the other positioned at a distance too long for a bonding interaction (~2.7 Å). The bond distances involving the diketonate ligand in  $\mathbf{1}_{b}$  are similar to those in  $\mathbf{1}_{Cl}$ . However, there is a notable difference between these two anion-coordinated structures. Although each anion coordinates in the axial position of the square pyramid, the benzoate ligand in  $\mathbf{1}_{b}$  forms a significantly shorter bonding interaction (2.139 Å) with the Cu(II) center than does the chloride in  $\mathbf{1}_{Cl}$  (2.448 Å). This suggests that benzoate is more strongly coordinated to the Cu(II) center,

which is supported by calculated enthalpies of binding  $(\Delta H(\text{benzoate}) = -7.1 \text{ kcal/mol}; \Delta H(\text{Cl}^-) = +3.4 \text{ kcal/mol})$ . As in  $\mathbf{1}_{\text{Cl}}$  the presence of the coordinated anion in  $\mathbf{1}_{\text{b}}$  lowers the enthalpy associated with the activation barrier for O<sub>2</sub> binding to give a peroxo intermediate (Figure 12). The Cu(II)



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Figure 12. Plots of calculated enthalpy vs reaction coordinate for steps in the reactions of 1,  $1_{Cb}$  and  $1_{b}$  with  $O_2$ .

coordination environments in the anion-coordinated structures of  $TS1_x$  and  $1-P_x$  (X = Cl, b) are similar (Figures S23 and S24 and Tables S13 and S14), with the coordinated chloride or benzoate anion positioned in the equatorial plane trans to the pyridyl donor. In  $TS1_x$  for both anions, the chlorodiketonate ligand is bound in a monodentate fashion in an axial position. Formation of the peroxo intermediate in both cases results in loss of the Cu-O(diketonate) carbonyl interaction. Anion coordination stabilizes the bridging peroxo intermediate, with the greatest stabilization found for  $1-P_{\rm b}$  (Figure 12). We note that trapping of a peroxo intermediate is anticipated to be difficult for the parent compound because generation of 1-P is predicted to be slower than its decay to 1-T<sub>ph</sub>. A similar situation is found for 1-P<sub>Cl</sub>. In both cases the peroxo species is not predicted to accumulate. Only in the case of benzoate (1- $P_{\rm b}$ ) is this not the case, and ongoing studies are being performed to probe for the possible identification of this peroxo species.

Significantly, chloride is far more efficient than benzoate in lowering the barrier associated with O–O bond cleavage coupled to chloride release  $(TS2_x)$  in the peroxo intermediate. As shown in Figure 12, the barrier for this second step is 24.7 kcal/mol in the absence of added anion (1-P), 20.7 kcal/mol in the presence of benzoate  $(1-P_b)$ , and only 11.6 kcal/mol starting from  $1-P_{CI}$ . Thus, chloride coordination to 1 significantly lowers *both* the TS1 and TS2 barriers, giving the lowest-energy catalytic pathway overall.

Similar to the 1-P and 1-P<sub>CI</sub> systems, for 1-P<sub>b</sub> a heterolytic pathway in which a phenyl appendage fragment of the chelate ligand is oxidized to arene oxide was also found (TS2<sub>b</sub> Ph and T<sub>b</sub>Ph; Figures S25 and S26 and Tables S15 and S16). However, in analogy to the 1-P<sub>CI</sub> system, oxidation of the anionic ligand (here to perbenzoate) is predicted to be faster than oxidation of

the phenyl fragment of the chelate  $(TS2_{b_Ph} \text{ lies 5.9 kcal/mol} \text{ above } TS2_b; Figure 12).$ 

The long, slow decay of the  $\pi \to \pi^*$  absorption feature of 1 in the presence of 1 equiv of added benzoate (Figure 13)



**Figure 13.** Plots of absorbance vs time for the reactions of 1 with  $O_2$  in the presence of 0.75 and 1.0 equiv of  $Bu_4NOC(O)Ph$  and a mixture containing 1.0 equiv of  $Bu_4NOC(O)Ph$  to which 0.2 equiv of  $Bu_4NCl$  was added after 13 395 s.

reflects the stronger coordination of this anion (vs chloride) and suggests that the reaction needs to proceed to an extent that a sufficient amount of free chloride ion is available ( $\sim 20\%$ decrease in absorption; Figure 13) to compete with benzoate for coordination to the Cu(II) center. In other words, the maximal rate of reaction for 1, via the lowest-energy "chloride" pathway, can be achieved only when a sufficient amount of chloride is generated to compete with the benzoate as a ligand. From the experimentally determined log K values,  $\Delta G$  can be calculated to be -2.51 and -3.82 kcal/mol for chloride and benzoate binding, respectively. This 1.31 kcal/mol difference in favor of benzoate is small relative to the computed catalytic effect of chloride ion, which is  $-9.0 \text{ kcal/mol} (TS1 \rightarrow TS1_{Cl})$ . Hence, even though benzoate binds more strongly to copper, still a small fraction of benzoate will be replaced by chloride, and the resulting complex will react faster with O<sub>2</sub>. In other words, the reactive species does not have to prevail in the reaction mixture. It is enough if the reactivity more than offsets the energy penalty connected with generating this species. If this idea is correct, addition of chloride ion to a solution containing 1 in the presence of 1 equiv of benzoate ion should "rescue" the system and induce a rapid decay process. As shown in Figure 13, addition of  $Bu_4NCl$  (0.2 equiv) to an  $O_2$ -purged CH<sub>3</sub>CN solution of 1 containing 1 equiv of benzoate ion indeed does produce the expected rapid decay, indicating that the chloride-coordinated lower-energy pathway is accessed.

To probe whether the effect of benzoate ion identified in the  $6\text{-Ph}_2\text{TPA}\text{-ligated complex 1}$  is retained in the reactivity of the simpler bpy-ligated complex 3, this complex was also treated with 1 equiv of Bu<sub>4</sub>NOC(O)Ph, and its O<sub>2</sub> reactivity was examined. Comparison of the rate of decay of this mixture versus that of 3 in the absence of added benzoate revealed behavior similar to that found for 1 (Figure S27).

### DISCUSSION AND CONCLUSIONS

There is a need to understand the ways in which anions can affect the O2 activation and O-O bond cleavage chemistry involved in Cu(II)/O2-mediated reactions that result in aliphatic C-C bond cleavage. Screening approaches are generally performed to optimize product yields in such reactions, and less attention is given to understanding why various Cu(II) salts give dramatically different results. The development of an understanding of the influence of anions on  $Cu(II)/O_2$  chemistry may provide a more rational approach to enable more economical and environmentally friendly syntheses of important precursor compounds (e.g.,  $\alpha$ -keto esters and 1,2-diketones) for the pharmaceutical industry. In this regard, we note that while prior studies of aliphatic carbon-carbon bond cleavage in the presence of copper, oxygen, and chloride ion have been reported, no specific anion effects were noted.<sup>15</sup>

Significantly, coordination of a chloride or benzoate anion to the copper center of 1 lowers the barrier associated with the formation of a five-coordinate  $Cu(II)-O_2^-$  species in TS1<sub>x</sub>. The most notable structural impact associated with anion binding to 1 (to form  $\mathbf{1}_X)$  involves the weakening of interactions between the Cu(II) center and the phenylappended pyridyl donors. This makes structural changes within the copper coordination sphere associated with the formation of TS1<sub>x</sub> and O<sub>2</sub> binding less unfavorable. This is somewhat akin to the halide effect reported for the non-heme iron halogenase HctB. In the presence of saturating amounts of chloride, the rate of oxidative reactivity of this enzyme is increased >200fold.<sup>16</sup> This rate enhancement was attributed to chloride coordination to the Fe(II) center, which results in a conformational change in the enzyme structure that facilitates proper binding of the substrate and formation of the catalytically competent enzyme-substrate complex for O<sub>2</sub> binding.

Notably, the degree to which the  $TS1_x$  barrier is lowered does not depend on the nature of the anion, with chloride and benzoate producing similar effects (lowering by ~9-10 kcal/ mol) despite their differences in basicity and enthalpy of coordination to the Cu(II) center. The nature of the anion instead more significantly impacts the energetics associated with the O-O bond cleavage reaction, which results in the production of triketone and oxyanion intermediates from the peroxide intermediate  $(1-P_X \rightarrow 1-T_X)$ . Here the coordinated anion provides the electron pair needed for heterolytic O-O bond cleavage. The significantly lower barrier for chloride versus benzoate is a consequence of the enhanced stabilization of the benzoate-coordinated peroxo species  $(1-P_b)$  and the higher TS2<sub>b</sub> barrier associated with peroxybenzoate formation. Our experimental results are consistent with the computations in that the maximal rate of reaction for 1 is achieved only under conditions wherein chloride coordination is present, thus enabling access to the TS1<sub>Cl</sub>/TS2<sub>Cl</sub> pathway.

The effect of carboxylate coordination in this system is notably different from that observed previously in a synthetic model system for quercetin dioxygenase (QDO).<sup>17</sup> Specifically, carboxylate ligands of increasing steric bulk have been shown to *enhance* the reactivity of an Fe(III)-containing model system for QDO. In this case, a trans orientation of the carboxylate donor and the flavonolato ligand on the Fe(III) center was proposed to facilitate monodentate coordination of the latter. This results in enhanced electron density within the flavonolato ligand, which makes it a better reductant, thus enhancing the rate of the reaction with  $O_2$ . In the case of the reactivity of 1, the individual steps involving  $O_2$  binding and O–O cleavage are affected differently depending on the nature of the anion.

Overall, the studies reported herein offer unprecedented new insight into how anions associated with a copper center can influence the  $O_2$  reactivity in a Cu(II)/ $O_2$ -mediated aliphatic carbon-carbon bond cleavage reaction. The use of chelated Cu(II) complexes has enabled spectroscopic studies of welldefined species wherein anion adducts can be spectroscopically investigated. The similarity of the chemistry of bpy-ligated complex 3 to that of 1 in terms of the effect of coordinated anions on the  $O_2$  reactivity indicates that Cu(II) complexes supported by simple bidentate ligands may be useful in future mechanistic studies of aliphatic C-C bond cleavage processes.

# EXPERIMENTAL SECTION

**General Methods.** All reagents were obtained from commercial sources and were used without further purification unless otherwise stated. Bu<sub>4</sub>NOC(O)Ph (>99%) was purchased from Sigma-Aldrich. Solvents were dried according to published procedures and purified by distillation under N<sub>2</sub> prior to use.<sup>18</sup> The chelate ligand N,N-bis((6-phenyl-2-pyridyl)methyl)-N-((2-pyridyl)methyl)amine (6-Ph<sub>2</sub>TPA)<sup>19</sup> and the diketone 2-chloro-1,3-diphenylpropane-1,3-dione<sup>20</sup> were prepared according to previously published procedures. All manipulations were carried out in an MBraun Unilab glovebox with a N<sub>2</sub> atmosphere unless otherwise noted.

**Physical Methods.** UV–vis data were collected on a Cary 50 spectrometer at 25 °C. Kinetic measurements were performed at 25 °C in 1 mm path length quartz cells with Teflon stopcocks. FTIR spectra were collected on a Shimadzu FTIR-8400 spectrometer as KBr pellets. CO and  $CO_2$  gases were detected and quantified using an Agilent 3000A micro gas chromatograph with molecular sieve and Plot U columns and a thermal conductivity detector. Mass spectral data for the metal complexes were collected by the Mass Spectrometry Facility at the University of California, Riverside. Elemental analyses were performed by Robertson Microlit Laboratories (Ledgewood, N.J.).

**EPR Spectroscopy.** X-band EPR spectra were recorded with a Bruker EMX EPR spectrometer, equipped with a Bruker ER-4116 dual-mode resonator, on 0.5 mM solutions in 80:20 CH<sub>3</sub>CN/toluene that were thoroughly degassed by multiple freeze–pump–thaw cycles. Temperature control was maintained using an Oxford ESR900 flow-through liquid helium cryostat. Other conditions, unless otherwise noted:  $\nu_{MW}$  = 9.68 GHz (2 mW); 2 G field modulation (100 kHz); receiver gain = 50 000; time constant/conversion time = 82 ms; 2–4 sweeps per spectrum.

**Syntheses.** *Caution!* Perchlorate compounds containing organic ligands are potentially explosive and should be handled with extreme care and in small quantities (<50 mg).<sup>21</sup>

 $[(bpy)Cu(PhC(O)CCIC(O)Ph)(CIO_4)]$  (3). Under an inert atmosphere,  $Cu(ClO_4)_2 \cdot 6H_2O$  (50 mg, 0.14 mmol) was dissolved in CH<sub>3</sub>CN (2 mL) and added to 2,2'-bipyridine (21.1 mg, 0.14 mmol), and the resulting mixture was stirred for 30 min. 2-Chloro-1,3-diphenylpropane-1,3-dione (34.9 mg, 0.14 mmol) was dissolved in Et<sub>2</sub>O (2 mL) and added to solid lithium bis(trimethylsilyl)amide (22.6 mg 0.14 mmol), and the mixture was stirred for 5 min, resulting in a paleyellow solution. The solutions were then combined and stirred for 18 h to produce a green solution. The solvent was removed under reduced pressure, and the crude material was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered through a glass wool/Celite plug. The solvent was then removed under reduced pressure, and crystals suitable for X-ray diffraction were grown by vapor diffusion of Et<sub>2</sub>O into a CH<sub>3</sub>CN solution (22.1 mg, 28% yield). Elemental analysis (%) calcd for C<sub>25</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub>Cl<sub>2</sub>Cu·0.75CH<sub>3</sub>CN: C, 52.38; H, 3.36; N, 6.34. Found: C, 52.07; H, 3.14; N, 6.64. ESI/APCI MS: m/z calcd for  $C_{25}H_{18}N_2O_2ClCu$ , 476.0347 [M - ClO<sub>4</sub>]<sup>+</sup>; found, 476.0343. UVvis  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 248 (17 360), 299 (21 065), 310 (19 992),

357 (10124). FTIR (KBr, cm<sup>-1</sup>): 1529, 1338, 1115 ( $\nu_{CIO_4}$ ), 619 ( $\nu_{CIO_4}$ ).

[(6-Ph<sub>2</sub>TPA)Cu(O<sub>2</sub>CPh)]ClO<sub>4</sub> (4). Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (27.4 mg, 7.74 mmol) was dissolved in CH<sub>3</sub>CN (5 mL) and added to 6-Ph<sub>2</sub>TPA (32.8 mg,7.4 mmol). The resulting blue solution was stirred for 30 min, at which time all of the solids had completely dissolved. The solution was then added to solid sodium benzoate (10.7 mg, 7.4 mmol), and the resulting mixture was stirred overnight. Removal of the solvent under reduced pressure yielded a blue-green residue, which was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered through a glass wool/Celite plug. Following removal of the solvent under reduced pressure, recrystallization of the residue from CH<sub>2</sub>Cl<sub>2</sub> via vapor diffusion with Et<sub>2</sub>O yielded blue/green crystals suitable for X-ray diffraction (45.1 mg, 84% yield). Elemental analysis (%) calcd for C<sub>37</sub>H<sub>31</sub>N<sub>4</sub>O<sub>6</sub>ClCu·0.2H<sub>2</sub>O: C, 60.20; H, 4.41; N, 7.80. Found: C, 60.21; H, 4.44; N, 7.52. ESI/APCI MS: m/z calcd for C<sub>37</sub>H<sub>31</sub>N<sub>4</sub>O<sub>2</sub>Cu, 626.1738 [M – ClO<sub>4</sub>]<sup>+</sup>; found, 626.1766. UV–vis  $\lambda_{max}$  nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 282 (19 770). FTIR (KBr, cm<sup>-1</sup>): 1602, 1443, 1094 ( $\nu_{ClO_4}$ ), 697 ( $\nu_{ClO_4}$ ).

**Kinetic Studies.** A 1 mM solution of 1 or 3 in CH<sub>3</sub>CN was made in an inert-atmosphere glovebox. Aliquots of the solutions were transferred to a 1 mm quartz cuvette and purged with O<sub>2</sub> for 30 s. The sealed cuvette was inverted three times to mix. This purge and mixing process was repeated, and then the respective  $\pi - \pi^*$  absorption bands for 1 and 3 were monitored by UV-vis as a function of time.

Anion Binding Studies. To a solution of 1 or 3 in CH<sub>3</sub>CN (1.0 mM for the  $\pi$ - $\pi$ \* absorption band; ~6.5 mM for d-d transitions) was added Bu<sub>4</sub>NX (X = Cl, OC(O)OPh) dissolved at various concentrations in CH<sub>3</sub>CN under an inert atmosphere. The total volume of each final solution was 400  $\mu$ L. Each solution was then transferred to a 1 mM quartz cuvette equipped with a stopcock, and the absorption features were measured under anaerobic conditions.

**X-ray Crystallography.** A clear, intense-green platelike crystal of 3 of approximate dimensions 0.168 mm  $\times$  0.168 mm  $\times$  0.392 mm and a clear, blue platelike crystal of 4 of approximate dimensions 0.112 mm  $\times$  0.308 mm  $\times$  0.434 mm were mounted using a viscous oil. Data were collected using a Nonius Kappa CCD diffractometer (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å).

[(bpy)Cu(PhC(O)CClC(O)Ph) (ClO<sub>4</sub>)] (3). A total of 986 frames were collected and subsequently integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 52 276 reflections to a maximum  $\theta$  angle of 30.03° (0.71 Å resolution), of which 7570 were independent (average redundancy 6.906, completeness = 100.0%,  $R_{\rm int}$  = 3.99%,  $R_{\rm sig}$  = 2.91%) and 6055 (79.99%) were greater than  $2\sigma(F^2)$ . The final cell constants, a = 9.0564(3) Å, b = 20.6815(8) Å, c = 14.3598(5) Å,  $\beta = 106.036(2)^\circ$ , and V = 2584.93(16) Å<sup>3</sup>, are based upon the refinement of the XYZ centroids of 9892 reflections above  $20\sigma(I)$  with 4.793° <  $2\theta < 59.82^\circ$ . Data were corrected for absorption effects using the multiscan method (SADABS). The ratio of minimum to maximum apparent transmission coefficients (based on crystal size) were 0.6720 and 0.8370.

The structure of **3** was solved and refined using the Bruker SHELXTL software package in space group  $P2_1/n$  with Z = 4 for the formula unit,  $C_{27}H_{21}Cl_2CuN_3O_6$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 353 variables converged at  $R_1 = 3.42\%$  for the observed data and  $wR_2 = 8.70\%$  for all data. The goodness of fit was 1.033. The largest peak in the final difference electron density synthesis was 0.414 e/Å<sup>3</sup> and the largest hole was  $-0.398 e/Å^3$ , with a root-mean-square (RMS) deviation of 0.066 e/Å<sup>3</sup>. On the basis of the final model, the calculated density was 1.588 g/cm<sup>3</sup> and F(000) was 1260e.

[(6-Ph<sub>2</sub>TPA)Cu(O<sub>2</sub>CPh)]ClO<sub>4</sub> (4). A total of 1108 frames were collected and integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 89 920 reflections to a maximum  $\theta$  angle of 27.88° (0.76 Å resolution), of which 7757 were independent (average redundancy 11.592, completeness = 100.0%,  $R_{\rm int}$  = 3.17%,  $R_{\rm sig}$  = 1.81%) and 6768 (87.25%) were greater than  $2\sigma(F^2)$ . The final cell

constants, a = 11.0622(3) Å, b = 24.4722(6) Å, c = 12.2273(3) Å,  $\beta = 100.6170(10)^{\circ}$ , and V = 3253.46(14) Å<sup>3</sup>, are based upon the refinement of the *XYZ* centroids of 9880 reflections above  $20\sigma(I)$  with 4.750° <  $2\theta$  < 55.83°. Data were corrected for absorption effects using the multiscan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.889. The calculated minimum and maximum transmission coefficients (based on crystal size) were 0.7200 and 0.9150.

The structure of 4 was solved and refined using the Bruker SHELXTL software package in space group  $P2_1/c$  with Z = 4 for the formula unit,  $C_{37}H_{31}$ ClCuN<sub>4</sub>O<sub>6</sub>. The final anisotropic full-matrix least-squares refinement on  $F^2$  with 442 variables converged at  $R_1 = 2.84\%$  for the observed data and  $wR_2 = 7.08\%$  for all of the data. The goodness of fit was 1.030. The largest peak in the final difference electron density synthesis was 0.337 e/Å<sup>3</sup> and the largest hole was  $-0.340 \text{ e/Å}^3$ , with an RMS deviation of 0.051 e/Å<sup>3</sup>. On the basis of the final model, the calculated density was 1.483 g/cm<sup>3</sup> and F(000) was 1500e.

**Computational Details.** The computational model consisted of the full cationic part of the salt, i.e., the Cu(II) ion complexed with 6-Ph<sub>2</sub>TPA and the chlorodiketonate anion. To investigate the catalytic role of chloride anion, a model with chloride bound in the first coordination sphere was also used to study the initial steps of the reaction. The chloride was placed at the coordination site liberated by dissociation of either the pyridyl arm or a phenyl-appended pyridyl arm (N<sub>PhPy</sub>) of the 6-Ph<sub>2</sub>TPA ligand. The two variants of the charge-neutral complex had very similar stabilities (within 0.3 kcal/mol). Because of the weak interaction between the copper center and the N<sub>PhPy</sub> donors of the 6-Ph<sub>2</sub>TPA ligand, which allows easy isomerization of the complex, the two variants converged to the same mechanism for chlorodiketonate anion oxidation. The model with benzoate bound to copper ion was constructed by replacement of chloride in  $1-S_{CI}$  with benzoate.

Geometries of stationary points and their harmonic frequencies were obtained with the B3LYP-D2 exchange-correlation functional, which includes empirical corrections for dispersion,<sup>22</sup> and a double- $\zeta$ basis set consisting of LANL2DZ for copper and 6-31G for other elements (BS1). The final electronic energy was computed with the B3LYP-D3<sup>23</sup> or TPSSh-D3<sup>24</sup> functional using a larger basis set of triple- $\zeta$  quality that combined the lacv3p+ basis for copper with the ccpVTZ(-f) basis set for other elements (BS2). The two functionals gave very similar energy profiles along the reaction coordinate, and hence, in the discussion we have focused on the B3LYP-D3 results. For stationary points, corrections to the energy due to solvent (acetonitrile) were computed at the B3LYP/BS1 level with the polarizable continuum model using the integral equation formalism (IEFPCM) as implemented in Gaussian 09. The reported enthalpies were computed by combining the electronic energy computed with BS2 with the solvent corrections and corrections to enthalpy (298.15 K, 1 atm) computed at the B3LYP/BS1 level using the harmonic approximation. This approach treats the reactants (i.e., the complex and O2 molecules) as ideal gas particles, and hence, the entropy effects connected with association of molecules in real solvent cannot be expected to be realistically reproduced. For this reason, we have reported enthalpies instead of Gibbs free energies. For species with antiferromagnetic coupling between unpaired electrons, the electronic energy was corrected with the procedure proposed by Yamaguchi and co-workers.<sup>25</sup> The reactive surface corresponds to the lowest-energy doublet spin state. For excited-state calculations, TD-DFT with CAM-B3LYP functional was used. To compute the adiabatic excitation energy to the lowest LMCT state of species 1, both the ground state and the LMCT state (root #2) were optimized in vacuum employing BS1. The final excitation energy was computed with the use of BS2 and the IEFPCM solvent model. All of the computations were done with the spin-unrestricted formalism using the Jaguar<sup>26</sup> and Gaussian  $09^{27}$  suites of programs.

# ASSOCIATED CONTENT

# **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b00456.

Rose–Drago plots for reactions of 1 and 3 with chloride and 1 with benzoate; absorption and EPR spectra of 1 in the presence of excess chloride and benzoate; modeled absorption spectra and speciation plots; structural representations and tables of bond distances for calculated transition states and intermediates for the reactions of 1 with  $O_2$  in the presence of no added anion, chloride, or benzoate; mass spectral data for 1 and 3 upon treatment with  $O_2$ ; absorbance versus time data for the reaction of 3 with  $O_2$ ; and coordinates of geometryoptimized structures (PDF)

Crystallographic data for 3 and 4 (CIF)

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#### Notes

The authors declare no competing financial interest.

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