Published in final edited form as:

Dalton Trans. 2017 February 21; 46(8): 2551–2558. doi:10.1039/c6dt04427a.

Sterically Directed Nitronate Complexes of 2,6-Di-*tert*-Butyl-4-Nitrophenoxide with Cu(II) and Zn(II) and Their H-Atom Transfer Reactivity

Thomas R. Porter^{a,b}, Ellen C. Hayes^a, Werner Kaminsky^a, and James M. Mayer^{a,c}

^aDepartment of Chemistry, University of Washington, Box 351700, Seattle, Washington 98195-1700, United States

^bLaboratoire d'Electrochimie Moléculaire, Université Paris Diderot, Bâtiment Lavoisier, 15 rue Jean de Bâif, 75205 Paris Cedex 13, France

^cDepartment of Chemistry, Yale University, 225 Prospect Street, New Haven, Connecticut 06520, United States

Abstract

The bulky 2,6-di-*tert*-butyl-4-nitrophenolate ligand forms complexes with $[\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}]^+$ and $[\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}]^+$ binding via the nitro group in an unusual nitronato-quinone resonance form ($\text{Tp}^{\text{tBu}} = \text{hydro-}tris(3\text{-}tert\text{-butyl-pyrazol-1-yl})\text{borate}$). The Cu complex in the solid state has a five-coordinate κ^2 -nitronate structure, while the Zn analogue has a four-coordinate κ^1 -nitronate ligand. 4-Nitrophenol, without the 2,6-di-*tert*-butyl substituents, instead binds to $[\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}]^+$ through the phenolate oxygen. This difference in binding is very likely due to the steric difficulty of binding a 2,6-di-*tert*-butyl-phenolate ligand to the $[\text{Tp}^{\text{tBu}}\text{M}^{\text{II}}]^+$ unit. $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}(\kappa^2\text{-O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O})$ reacts with the hydroxylamine TEMPO-H (2,2,6,6-tetramethylpiperidin-1-ol) by abstracting a hydrogen atom. This system thus shows an unusual sterically enforced transition metal-ligand binding motif and a copper-phenolate interaction that differs from what is typically observed in biological and chemical catalysis.

Graphical Abstract

Correspondence to: James M. Mayer.

Electronic Supplementary Information (ESI) available: Crystallographic data and additional characterization of complexes and reactions. See DOI: 10.1039/x0xx00000x

Introduction

Chemical reactions between copper(II) and phenols or phenol derivatives are widespread and significant in a variety of processes in chemistry and biology. The enzyme tyrosinase, for example, uses a di-copper containing active site to oxidize tyrosine to dopaquinone in the first biosynthetic step of the production of the pigment melanin.¹ In chemistry, copper catalysts are used for aerobic oxidations of phenols and naphthols, for instance in the production of BINOLs (1,1'-bis-2,2'-naphthols).²

Many of these reactions involve a copper(II) phenoxide intermediate,^{2b} in which the copper ion activates the phenoxide ligand through radical delocalization onto the 2, 4, and 6 positions of the ring. This facilitates radical-radical coupling or O₂ addition reactions. Because of the importance of this motif, many examples of copper(II) phenoxide complexes have been reported and their reactivities have been well studied.³

We report here an example of a copper(II) complex that binds 2,6-di-*tert*-butyl-4-nitrophenoxide (O₂N^{*t*}Bu₂C₆H₂O[−]) *through the nitro group* (nitronate) rather than through the phenoxide oxygen, Tp^{*t*}BuCu^{II}(κ²-O₂N^{*t*}Bu₂C₆H₂O) (**1**) [Tp^{*t*}Bu = hydro-*tris*(3-*tert*-butylpyrazol-1-yl)borate]. The nitronato [−]O₂N=R unit binds κ² to the bulky [Tp^{*t*}BuCu^{II}]⁺ fragment, with the ligand better described as a nitronato-quinone rather than as a phenoxide (Scheme 1A). The [Tp^{*t*}BuZn^{II}]⁺ analog is similar except that the nitronate ligand binds κ¹ in this case. The same [Tp^{*t*}BuCu^{II}]⁺ complex binds the unsubstituted 4-nitrophenoxide through the phenolate oxygen. Similarly, Fujisawa, Moro-oka et al. reported some time ago that the slightly less bulky Tp^{*t*}PrCu unit makes phenoxide complexes with 2,6-di-methylphenoxide and even 2,6-di-*tert*-butyl-phenoxide ligands, although these species decomposed at ambient temperatures.^{3j} These results indicate that the unusual nitronate binding mode is the result of steric clash between the Tp^{*t*}Bu ligand and the *tert*-butyl groups of the phenol.

Transition metal-nitronate complexes have been reported for several different metals.⁴ The nitronate ligands are typically derived from α-deprotonated primary and secondary aliphatic nitro compounds (Scheme 1B). With only a one exception, these bind to metals in a κ² fashion.^{4a} To our knowledge, the examples reported here are the first transition metal complexes with nitronate ligands derived from a nitrophenol compound, a binding mode that appears to be sterically enforced. In addition to the structure and characterization of these compounds, we describe the ability of the Cu^{II}-κ²-nitronate-quinone complex to abstract H[•] from the hydroxylamine TEMPO-H (2,2,6,6-tetramethylpiperidin-1-ol).

Results and Discussions

Synthesis and Characterization of Tp^{*t*}BuCu^{II}(κ²-O₂N^{*t*}Bu₂C₆H₂O) (**1**)

Treatment of the previously described Tp^{*t*}BuCu^{II}-OCH₂CF₃⁵ with one equivalent of 2,6-di-*tert*-butyl-4-nitro-phenol (O₂N^{*t*}Bu₂C₆H₂OH) in toluene-*d*₈ resulted in a rapid colour change from red-orange to dark blue-green. The ¹H NMR spectrum of this reaction displayed new paramagnetically shifted resonances, the disappearance of free O₂N^{*t*}Bu₂C₆H₂OH and the appearance of free 2,2,2-trifluoroethanol, providing evidence of a protolytic ligand exchange reaction. When performed on a larger scale in benzene, removal of the solvent and 2,2,2-

trifluoroethanol in *vacuo* and crystallization from pentane at $-30\text{ }^{\circ}\text{C}$ yielded large green crystals of $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}(\kappa^2\text{-O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O})$ (**1**) (eq 1).

(1)

The X-ray crystal structure of (**1**) (Figure 1) indicates that indeed eq 1 does involve this protolytic displacement, but surprisingly the $\text{O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O}^-$ anion does not bind to the phenolic oxygen. Instead, the phenolate moiety binds κ^2 to the nitronate oxygens. The structure has a square pyramidal geometry about the Cu ion, with $\tau = 0.04$ where $\tau = 0$ for perfect square monopyramidal vs. $\tau = 1$ for perfect trigonal bipyramidal.⁶ Two of the Tp^{tBu} ligand pyrazole nitrogens bind to Cu(II) in the same square plane with the nitronato oxygens. The third Tp^{tBu} pyrazole nitrogen binds axially with a notably longer Cu–N bond distance.

The bond lengths show that the $\text{O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O}^-$ ligand is well described by the nitronato-quinone resonance form (Table 1, Scheme 1A). The dearomatization of the benzene ring is indicated by the contraction of the C23–C24 and C27–C26 bond distances, avg. 1.3575(6) Å, while the other four are lengthened: C24–C25 and C25–C26, avg. 1.481(7) Å, and C22–C23 and C22–C27, avg. 1.427(6) Å. The C25–O1 bond length of 1.236(7) is consistent with a quinone-like carbonyl bond.⁷

The nitronate C=N bond length of 1.333(6) Å in **1** is slightly longer than those of related metal- $\kappa^2\text{-O}_2\text{N}=\text{CR}_2$ complexes ($\text{R} = \text{H}, \text{CH}_3$), typically *ca.* 1.27–1.30 Å.⁴ Conversely, the N–O bonds are slightly shorter: avg. 1.300(7) Å vs. the typical *ca.* 1.32–1.34 Å.⁴ These deviations are consistent with some π -delocalization from the nitronate group back into the quinoidal substituent.

The X-band EPR spectrum of (**1**) at 120 K in a toluene glass can be modelled with rhombic g values of $g_x = 2.065$, $g_y = 2.156$ and $g_z = 2.318$ (Fig. 2). Compared to axial copper EPR powder spectra ($g_x = g_y$), the derivative powder EPR spectrum of (**1**) has diminished intensity in the high field region indicative of a rhombic spectrum. This has been observed in other five-coordinate copper nitrate compounds.⁸ Additionally, we modelled the diminished intensity as a 0.1 broadening around the g_y value due to g strain. This substantial distribution in the value of g_y is indicative of large structural changes such as interchange between the 5 and 4 coordinate structures (compare (**1**) and (**2**) in Figure 1) in solution. The large shifts of all three values away from the free electron g value indicate a $d_{x^2-y^2}$ ground state where the z direction most likely points along the long Cu–N4 axial bond.⁹ The largest copper hyperfine value $|A_z^{\text{Cu}}| = 128\text{ G}$ lies in the g_z direction. Nitrogen hyperfine coupling (not included in the simulation) along the g_x direction of $|A_z^{14\text{N}}| = 12\text{ G}$ is consistent with coupling to the coordinated pyrazole nitrogens which has been reported for the related $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-OAc}$ complex.¹⁰

The EPR spectrum of the structurally related $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-OAc}$ ($\tau = 0$; Fig. S1, Table S4)¹⁰ displays a similar spectrum with slightly larger $|A_z^{\text{Cu}}|$ and $|A^{\text{N}}|$ splitting than observed for **(1)** (142 vs 128 G and 14 vs 12 G). These results seem consistent with a greater spin delocalization onto the nitronate ligand in **(1)** that the acetate ligand in $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-OAc}$.

Synthesis and Characterization of $\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}(\kappa^1\text{-O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O})$ (**2**)

The addition of one equivalent of DBU (1,8-diazabicycloundec-7-ene) to a dichloromethane solution of equimolar $\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}\text{-OTf}$ and 2,6-di-*tert*-butyl-4-nitrophenol ($\text{O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{OH}$) results in the colourless solution turning light yellow (OTf = triflate, SO_3CF_3). Removal of the solvent followed by recrystallization from pentane at -30°C yielded large yellow crystals of $\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}(\kappa^1\text{-O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O})$ (**2**), the Zn(II) analogue of **(1)** (eq 2).

The X-ray structure of **(2)** displays a distorted tetrahedral Zn(II) center with 3 Zn–N bonds to the Tp^{tBu} ligand (Figure 1). In the fourth position, the $\text{O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O}^-$ ligand is bound in a similar nitronato-quinone form but through only one of the nitronate oxygens, unlike in **(1)**. The bond lengths of the ligand are similar to those observed in **(1)** except for the N–O bond distances which are much more asymmetric. The Zn(II) bound nitronate oxygen has a substantially longer N–O bond length than the unbound oxygen (N7–O2 = 1.3314(13) vs 1.2660(14) Å, respectively) (Table 1).

The geometry about Zn(II) deviates quite substantially from tetrahedral. A quantitative assessment of this distortion can be made using the pyramidalization normalization parameter, τ' . ($\tau' = [\Sigma(\text{L}_{\text{basal}}\text{-M-L}_{\text{basal}}) - \Sigma(\text{L}_{\text{basal}}\text{-M-L}_{\text{axial}})]/90$; $\tau' = 0$ for a perfect tetrahedral and $\tau' = 1$ for perfect trigonal monopyramidal).¹¹ The τ' value of **(2)** is 0.69 and is therefore better described as having trigonal monopyramidal geometry. This contrasts the much more tetrahedral structures reported by Parkin and others for related $\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}\text{-X}$ complexes, for which τ' values typically range from 0.3 to 0.4.¹²

Synthesis and Characterization of $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-OArNO}_2$ (**3**)

Analogous to the synthesis of **(1)**, the addition of one equivalent of 4-nitrophenol (HOArNO_2) to $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-OCH}_2\text{CF}_3$ in benzene resulted in a rapid colour change from orange-red to green-brown. After removing the solvent in *vacuo*, the dark coloured solids were redissolved in diethyl ether and large brown and green dichroic crystals of $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-OArNO}_2$ (**3**) were grown from slow evaporation (eq. 3).

The X-ray structure of **(3)** shows a distorted tetrahedral geometry about copper ($\tau' = 0.62$) with 4-nitro-phenoxide bound to the metal center through the phenoxide oxygen (Figure 1, Table 1). The structure is quite similar to the previously reported and related 4-fluoro-phenoxide complex $\text{Tp}^{\text{tBu}}\text{PrCu}(\text{OC}_6\text{H}_4\text{F})$.^{3a}

The X-band EPR spectrum of **(3)** in a toluene glass at 120 K was modelled with rhombic g values of $g_z = 2.0021$, $g_y = 2.145$, and $g_x = 2.320$ (Fig. 2). The g_z value nearly equals the free electron g value ($g_e = 2.0023$) indicating this molecule is in the d_{z^2} ground state.⁹ The crystal structure reveals a significant distortion of the geometry such that N2 and O1 are nearly *trans* to each other ($\approx 160^\circ$). The direction of the g_z axis (and molecular z axis) is less clear without further experiments for **(3)**; however, the d_{z^2} ground state would be favoured if z lies along this N2-Cu1-O1 axis making it rotated by $\approx 90^\circ$ compared to **1**. The largest copper hyperfine lies along the g_z axis with a value $|A_z^{\text{Cu}}| = 145$ G. Additional simulation parameters include copper hyperfine coupling of $|A_x^{\text{Cu}}|$ and $|A_y^{\text{Cu}}| < 13$ G; however, the exact experimental values are indistinguishable from the inhomogeneous broadening in the spectrum. Again, a large g strain of 0.03 in the g_y value was used for the simulation. Similar EPR spectra have been observed for related 4-coordinate $\text{TpCu}^{\text{II}}\text{-X}$ complexes with τ' values < 0.64 .^{5,13}

Attempts to Prepare 2,6-^tBu₂-phenoxyl complexes

In attempts to prepare copper(II) complexes with 2,6-^tBu₂-phenoxide ligands via radical coupling of a copper(I) precursor with stable organic radicals, the previously reported copper(I) dimer $[\text{Tp}^{\text{tBu}}\text{Cu}^{\text{I}}]_2$ ¹⁴ was treated with two equivalents of the stable 2,4,6-tri-*tert*-butylphenoxyl radical (^tBu₃ArO[•])¹⁵ in benzene(-*d*₆). No reaction was observed by UV/Vis or ¹H NMR spectroscopies (eq 4). The related 4-nitro-phenyl-phenoxyl radical (^tBu₂NPArO[•])¹⁶ also was similarly unreactive. This result is consistent with our previous report showing that treatment of $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-OCH}_2\text{CF}_3$ with ^tBu₂NPArOH yielded ½ $[\text{Tp}^{\text{tBu}}\text{Cu}^{\text{I}}]_2$, HOCH₂CF₃ and ^tBu₂NPArO[•] in partial yield with no formation of a Cu^{II}-nitronate complex observed.⁵

To prepare the related zinc complex, $\text{Tp}^{\text{Bu}}\text{Zn}^{\text{II}}\text{-OTf}$ was reacted with one equivalent of $t\text{Bu}_3\text{ArO-H}$ and DBU, analogous to equation 2 above. Upon workup, only $\text{Tp}^{\text{Bu}}\text{Zn}^{\text{II}}\text{-OTf}$ was recovered. Similar attempts with $\text{Tp}^{\text{Bu}}\text{Zn}^{\text{II}}\text{-Cl}$ and $t\text{Bu}_3\text{ArOLi}$ were also unsuccessful.

Spectroscopic and Electrochemical Measurements

The ^1H NMR spectra for all three complexes have equivalent $t\text{Bu}$ groups of their Tp^{Bu} ligands, indicating that they are fluxional on the NMR timescale. For the paramagnetic Cu^{II} complex (**1**), the resonances due to these $t\text{Bu}$ groups and the $t\text{Bu}$ groups from the nitronate ligand were the only signals observed and displayed the expected 3:2 peak integration. For complex (**3**), only the $t\text{Bu}$ groups from the Tp^{Bu} ligand were observed (Supporting Information Fig S4, S5). The optical spectrum of compound (**1**) displays a weak optical absorption at 796 nm ($\epsilon = 180 \text{ M}^{-1} \text{ cm}^{-1}$) while compound (**3**) has absorptions at 583 nm ($\epsilon = 430 \text{ M}^{-1} \text{ cm}^{-1}$), 667 nm ($\epsilon = 400 \text{ M}^{-1} \text{ cm}^{-1}$) and 830 nm ($\epsilon = 130 \text{ M}^{-1} \text{ cm}^{-1}$) (Supporting information Fig S2, S3).

The cyclic voltammogram (CV) of (**1**) in dichloromethane with 0.1 M $[\text{tBu}_4\text{N}][\text{PF}_6]$ (Supporting information fig. S6) shows irreversible electrochemical responses at both oxidizing and reducing potentials. The cathodic peak current, $E_{\text{c,a}}$, occurs at -0.84 V while the anodic peak current, $E_{\text{p,a}}$ occurs at 1.10 V (both $\text{vs Fc}^{+/0}$ and at 100 mV/s scan rates). Similar electrochemical irreversibility has been reported for related $\text{Tp}^{\text{Bu}}\text{Cu}^{\text{II}}\text{-X}$ complexes.^{5,14}

Reactivity with H-Atom Transfer Reagents

Combining 2.5 mM $[\text{Tp}^{\text{Bu}}\text{Cu}^{\text{I}}]_2$ with 2 equivalents of $\text{O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{OH}$ in benzene- d_6 or toluene- d_8 showed no reaction as determined by ^1H NMR. When one equivalent of the hydrogen atom acceptor, $t\text{Bu}_3\text{ArO}^\bullet$ was added to the same solution, a colour change from blue ($t\text{Bu}_3\text{ArO}^\bullet$) to green-brown occurred over roughly one hour. The optical trace of this reaction (Figure 3) displays clear isosbestic points and shows that (**1**) is generated in approximately 60% yield. Similarly, monitoring a related reaction by ^1H NMR showed 50% yield of (**1**) as well as signals for $t\text{Bu}_3\text{ArO-H}$ (~80%) and unreacted $\text{O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O-H}$ (~40%). All of the $t\text{Bu}_3\text{ArO}^\bullet$ is consumed during this reaction as determined from the optical spectrum of the completed reaction.

The reaction of (**1**) with the hydrogen atom donor TEMPO-H, each 12 mM in benzene, resulted in a colour change from green-brown to light pink over the course of an hour. ^1H NMR spectra showed quantitative formation of $\text{O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{OH}$ and $[\text{Tp}^{\text{Bu}}\text{Cu}^{\text{I}}]_2$. The optical spectrum of the same reaction showed a small absorption indicative of TEMPO radical at 460 nm, in essentially quantitative yield ($\Sigma_{460} = 11.1 \text{ M}^{-1} \text{ cm}^{-1}$ ¹⁷). The balanced reaction is therefore as described by equation 5.

(5)

Discussion

Sterically Directed Phenolate/Nitronate Linkage

The formation of the κ^2 -nitronate complex (**1**) from the 2,6-di-*t*-butyl-4-nitrophenol contrasts with the formation of the O-bond phenoxide complex (**3**) from the unhindered 4-nitrophenol. These results indicate that the preference for the nitronate coordination in (**1**) and (**2**) is the result of the steric clash between Tp^{Bu} *tert*-butyl groups and the 2,6-di-*tert*-butyl groups of the phenol. This is further supported by the inability to prepare related 2,6-di-*tert*-butyl-phenoxy complexes by ligand metathesis from $[\text{Tp}^{\text{Bu}}\text{Zn}^{\text{II}}]$ precursors or from $[\text{Tp}^{\text{Bu}}\text{Cu}^{\text{I}}]_2$ and bulky phenoxy radicals (eq 4).⁵

The reaction of $[\text{Tp}^{\text{Bu}}\text{Cu}^{\text{I}}]_2$ with $\text{O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O}-\text{H}$ and ${}^t\text{Bu}_3\text{ArO}^\bullet$ to give (**1**) in 50–60% yield likely proceeds by initial equilibration of the radicals, reaction 5. Based on the known O–H BDFEs for the two phenols in benzene,¹⁸ the equilibrium constant $K_5 = 3 \times 10^{-3}$ (eq 6). The self-exchange rate constant for ${}^t\text{Bu}_3\text{ArO}^\bullet + {}^t\text{Bu}_3\text{ArOH}$ is $95 \text{ M}^{-1} \text{ s}^{-1}$ in benzene,¹⁹ indicating that reaction 6 will be at equilibrium, with ca. 5% of the $\text{O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O}^\bullet$ radical. This transiently stable radical is known to have a lifetime suitable for EPR studies but irreversibly decomposes in minutes.²⁰ This suggests that $[\text{Tp}^{\text{Bu}}\text{Cu}^{\text{I}}]_2$ can react with the less sterically crowded nitro end of the $\text{O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O}^\bullet$ radical. This is consistent with the lack of reactivity with the oxygen end and with ${}^t\text{Bu}_3\text{C}_6\text{H}_2\text{O}^\bullet$ being due to sterics.

H-Atom Transfer Reactivity and Thermochemistry

Treatment of (**1**) with the hydrogen atom donor TEMPO–H results in net H^+/e^- transfer produces $\text{O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O}-\text{H}$, $1/2[\text{Tp}^{\text{Bu}}\text{Cu}^{\text{I}}]_2$, and TEMPO in quantitative yields. This reaction could proceed via several possible pathways, including concerted proton-electron transfer (CPET),²¹ protolytic ligand exchange followed by TEMPO dissociation, or phenoxy radical dissociation. Initial electron transfer (ET) or proton transfer (PT) are unlikely given the properties of (**1**) and TEMPO–H, following standard thermochemical arguments.^{18b}

Regardless of mechanism, the well-defined stoichiometry of this reaction provides thermochemical information about this system. Because this reaction proceeds quantitatively, it can be concluded that $\Delta G < 0$ under these conditions. Since this reaction

was carried out at concentrations much lower than standard state, entropy is expected to provide 1.3 kcal mol⁻¹ to G° here relative to standard state free energy, G° . A limit for G° of this reaction is thus expected to be $G^\circ \leq 1.3$ kcal mol⁻¹. With this limit, an ‘effective bond dissociation free energy (BDFE)²²’ of [Tp^tBuCu^I]₂ + O₂N^tBu₂C₆H₂O–H can be calculated using the known O–H bond strength of TEMPO–H (eq 7–9).

Summing (eq 7) and (eq 8) gives:

Since the O–H bond strength of O₂N^tBu₂C₆H₂O–H is known,¹⁶ this ‘effective BDFE’ limit can be used to extrapolate a thermodynamic limit for homolytically cleaving the Cu^{II}– κ^2 -O₂N=R chelating bond and forming ½ [Tp^tBuCu^I]₂.

Summing (eq 9) and (eq 10) gives:

(11)

It is important to note that this value encompasses both the free energy cost of homolytically cleaving the copper(II)-nitronate chelate as well as the free energy gained from the formation of the $[\text{Tp}^{t\text{Bu}}\text{Cu}^{\text{I}}]_2$ dimer. Dimer formation is likely a substantial free energy contribution to equation 11, since it was reported to be stable with respect to dissociation even at 362 K.¹⁴

The thermochemical analysis, even with these caveats, suggests that the loss of phenoxyl radical ($\text{O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O}^\bullet$) from **1** to form the copper dimer is not so endoergic. With the 2,4,6-tri-*tert*-butyl-phenoxyl radical that can only ligate through the phenoxide oxygen, the reaction analogous to reaction (11) actually favors the free phenoxyl radical ($\Delta G^\circ < 0$, eq 4).

The free radical is also more stable than the phenoxide or nitronate complex for the 4-nitrophenyl-2,6-di-*tert*-butyl phenoxyl radical¹⁶ (eq 4). In this case, the energetic cost to form the nitronate is evidently too large to de-aromatize two aromatic rings required for the quinonate structure.

This energetic analysis also provides a rationale for the facile decomposition of the $\text{Tp}^{PrPr}\text{Cu}$ -2,6-di-methyl-phenoxide and 2,6-di-*tert*-butyl-phenoxide complexes, as reported by Fujisawa, Moro-oka, et al.^{3j} The decomposition products that they identified are characteristic of phenoxyl radicals.

Conclusions

In the system described here, the steric bulk surrounding $[\text{Tp}^{t\text{Bu}}\text{Cu}^{\text{II}}]^+$ and $[\text{Tp}^{t\text{Bu}}\text{Zn}^{\text{II}}]^+$ units dictates the binding mode of nitrophenoxide ligand $\text{O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O}^-$. The 2,6-di-*tert*-butyl groups prevent coordination via the phenoxide oxygen, as indicated by unsuccessful attempts to prepare other 2,6-di-*tert*-butyl-phenoxide complexes. The Fujisawa, Moro-oka, et al. 2,6-di-*tert*-butyl-phenoxide complex with the slightly smaller di-*iso*-propyl-Tp ligand appears to be just on the cusp of thermochemical stability.^{3j} The 4-nitro-2,6-di-*tert*-butylphenoxide ligand has another alternative, to bind as a nitronate with a quinonoidal electronic structure. This binding mode is sterically much less crowded. In the absence of crowding, as in the simple 4-nitrophenolate, binding through the phenolate oxygen to $[\text{Tp}^{t\text{Bu}}\text{Cu}^{\text{II}}]^+$ is observed.

$\text{Tp}^{t\text{Bu}}\text{Cu}^{\text{II}}(\kappa^2\text{-O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O})$ (**1**) cleanly abstracts a hydrogen atom from the hydroxylamine TEMPO-H to form the Cu(I) dimer $\frac{1}{2}[\text{Tp}^{t\text{Bu}}\text{Cu}^{\text{I}}]_2$, $\text{O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{OH}$ and the nitroxyl radical TEMPO. Thermochemical analysis of this reaction provides limits for an 'effective BDFE' in this system and for loss of the phenoxyl radical from (**1**). This analysis provides a rationale for the copper-phenoxyl chemistry observed, including the new and

unusual sterically directed nitronate ligation mode of a bulky nitrophenoxide that differs from what is typically observed in biological and synthetic copper-phenol chemistries.

Experimental

Materials

Unless otherwise noted, all reactions were carried out in a nitrogen filled glovebox. All materials were purchased from Sigma-Aldrich and used without purification. Benzene- d_6 and toluene- d_8 were purchased from Cambridge Isotope Labs and dried over NaK prior to being vacuum distilled. Dichloromethane- d_2 was also purchased from Cambridge Isotope Labs and dried over CaH_2 prior to being vacuum distilled.

Other solvents were purchased from Fischer and dried using a “Grubbs type” Seca Solvent System installed by Glass-Contour. $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-OCH}_2\text{CF}_3$,⁵ $[\text{Tp}^{\text{tBu}}\text{Cu}^{\text{I}}]_2$,¹⁴ $\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}\text{-OTf}$,²³ $\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}\text{-Cl}$,²⁴ $\text{tBu}_2\text{-NO}_2\text{-ArO-H}$,²⁵ $\text{tBu}_3\text{ArO}^\bullet$,¹⁵ $\text{tBu}_2\text{NPArO}^\bullet$,¹⁶ and TEMPO-H ²⁶ were prepared following published synthetic protocols. All glassware was dried in an oven at 150 °C overnight and pumped into a nitrogen filled glovebox while still hot.

Instrumentation

All ^1H NMR spectra were collected on Bruker 300 and 500 MHz instruments. ^1H chemical shifts were referenced to TMS using the residual solvent peak. UV-visible absorption spectra were collected with a Hewlett-Packard 8453 diode array spectrometer and are reported as λ_{max} in nm (ϵ in $\text{M}^{-1}\text{cm}^{-1}$; uncertainties of *ca.* 10%). Cyclic voltammetry (CV) was performed using a CH instrument 600D potentiostat and the irreversible potentials given are ± 0.05 V. EPR spectra were collected with a Bruker EMX X-band spectrometer and simulations were performed using EasySpin.²⁷ g values are reported with ± 0.005 uncertainty. CHN elemental analysis was performed by Atlantic Microlabs, Inc., Norcross, GA.

Syntheses

hydro-*tris*(3-*tert*-butylpyrazol-1-yl)borate) copper(II) 3,5-*bis*(*tert*-butyl)-4-benzenone- κ^2 -nitronate, $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}(\kappa^2\text{-O}_2\text{N}^{\text{t}}\text{Bu}_2\text{C}_6\text{H}_2\text{O})$ (1)—To a ~5 mL solution of $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-OCH}_2\text{CF}_3$ (58.7 mg, 0.11 mmol) in benzene was added $\text{tBu}_2\text{-NO}_2\text{-ArOH}$ (27.1 mg, 0.11 mmol) with stirring. The solution quickly changed in colour from orange to blue-green. Removal of the solvent in vacuo gave dark green solid. Crystallization from pentane at -30 °C yielded 50 mg of large X-ray quality crystals (66 %). ^1H NMR (500 MHz, benzene- d_6) δ : 2.8 (broad, 27H), 1.0 (s, 18H); UV/Vis (toluene): 830 nm (180); Anal. Calcd. For $\text{C}_{35}\text{H}_{55}\text{CuN}_7\text{O}_3$: C, 60.47; H, 7.83; N, 14.01. Found: C, 60.74; H, 7.89; N, 14.16.

hydro-*tris*(3-*tert*-butylpyrazol-1-yl)borate) zinc(II) 3,5-*bis*(*tert*-butyl)-4-benzenone- κ^1 -nitronate, $\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}(\kappa^1\text{-O}_2\text{N}^{\text{t}}\text{Bu}_2\text{-C}_6\text{H}_2\text{O})$ (2)—To a ~5 mL dichloromethane solution of $\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}\text{-OTf}$ (101.3 mg, 0.17 mmol) was added dropwise a ~2 mL dichloromethane solution of DBU (25.9 mg, 0.17 mmol) and 2,6-di-*tert*-butyl-4-nitro phenol (42.7 mg, 0.17 mmol) with stirring. Upon addition, the solution turned from colourless to yellow. After 10 minutes the solvent was removed in vacuo and the remaining

solid was redissolved in a minimum amount of pentane and filtered. Large yellow X-ray quality crystals grew upon standing at $-30\text{ }^{\circ}\text{C}$ (73.1 mg, 62%). ^1H NMR (500 MHz, CD_2Cl_2) δ : 7.74 (s, 2H), 7.61 (d, $^3J_{\text{HH}} = 2.3\text{ Hz}$, 3H), 6.12 (d, $^3J_{\text{HH}} = 2.3\text{ Hz}$, 3H), 1.33 (s, 27H), 1.31 (s, 18H). Anal. Calcd. For $\text{C}_{35}\text{H}_{54}\text{BN}_7\text{O}_3\text{Zn}$: C, 60.31; H, 7.81; N, 14.07. Found: C, 60.42; H, 7.59; N, 14.20.

hydro-*tris*(3-*tert*-butypyrazol-1-yl)borate) copper(II) 4-nitrophenolate (3)—To a $\sim 5\text{ mL}$ dichloromethane solution of $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-OCH}_2\text{CF}_3$ (62.2 mg, 0.114 mmol) was added a $\sim 2\text{ mL}$ dichloromethane solution of 4-nitro-phenol (15.9 mg, 0.114 mmol). Upon addition, the solution turned from orange to brown-green. After the solvent was removed in vacuo, the resulting solids were redissolved in diethyl ether, filtered over Celite and crystallized by slow evaporation yielding green/brown dichroic crystals of (3) (65.5 mg, 98%). ^1H NMR (300 MHz, CD_2Cl_2) δ : 7.6 (broad, 27H). UV/Vis (toluene): 583 (430), 667 (400), 830 (130). Anal. Calcd. For $\text{C}_{27}\text{H}_{38}\text{BCuN}_7\text{O}_3$: C, 55.63; H, 6.57; N, 16.82. Found: C, 55.44; H, 6.56; N, 16.85.

Reactions

Representative NMR Reaction Procedure—A TEMPO-H solution (300 mL, 24 mM, benzene- d_6) was added dropwise to a solution of $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-O}_2\text{N}^{\text{tBu}}\text{C}_6\text{H}_2\text{O}$ (300 mL, 24 mM, benzene- d_6) with stirring. The resulting solution was transferred to a J. Young NMR tube and stored at room temperature in the dark until the reaction had reached completion.

Representative UV/Vis Procedure—To a septum-capped 1 cm path length quartz cuvette containing a 2.5 mL benzene solution of $[\text{Tp}^{\text{tBu}}\text{Cu}^{\text{I}}]_2$ (3 mM) and $^{\text{tBu}}\text{Bu}_2\text{NO}_2\text{ArO-H}$ (6 mM) was added a 0.5 mL benzene solution of $^{\text{tBu}}\text{Bu}_3\text{ArO}^{\bullet}$ (30 mM) from a gas-tight syringe (Final concentrations 2.5, 5, and 5 mM for $[\text{Tp}^{\text{tBu}}\text{Cu}^{\text{I}}]_2$, $^{\text{tBu}}\text{Bu}_2\text{NO}_2\text{ArO-H}$, and $^{\text{tBu}}\text{Bu}_3\text{ArO}^{\bullet}$, respectively). The cuvette was inverted several times prior to beginning optical measurements to ensure complete mixing had occurred.

Attempts to prepare “ $\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}\text{-OAr}^{\text{tBu}}_3$ ”

Attempt 1—To a $\sim 5\text{ mL}$ dichloromethane solution of $\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}\text{-OTf}$ (73.1 mg, 0.11 mmol) was added dropwise a $\sim 2\text{ mL}$ dichloromethane solution of DBU (18.6 mg, 0.11 mmol) and 2,4,6-tri-*tert*-butyl phenol (32.0 mg, 0.11 mmol) with stirring. After stirring for one hour, the solvent was removed in vacuo, the resulting solids taken up in pentane, filtered over Celite. After removal of the solvent, the crude white solid remaining was identified as the starting Zn complex, $\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}\text{-OTf}$, by ^1H NMR.

Attempt 2— $\text{LiOAr}^{\text{tBu}}_3\text{-THF}$ was prepared *in situ* by the addition of one equivalent of lithium *bis*(trimethylsilyl)amide (LiHMDS) (22.2 mg, 0.13 mmol) to $^{\text{tBu}}\text{Bu}_3\text{ArOH}$ (34.8 mg, 0.13 mmol) in $\sim 3\text{ mL}$ THF. Addition of this solution to a $\sim 5\text{ mL}$ THF solution containing $\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}\text{-Cl}$ (64.4 mg, 0.13 mmol) was carried out with stirring. After 1 hour, the solvent was removed in vacuo, the solids were taken up in toluene, filtered over Celite, and crystallized at $-30\text{ }^{\circ}\text{C}$. The resulting colourless crystals were found to be $\text{LiOAr}^{\text{tBu}}_3\text{-THF}$ and the mother liquor from crystallization was found to contain $\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}\text{-Cl}$ and $\text{LiOAr}^{\text{tBu}}_3\text{-THF}$ as determined by ^1H NMR.²⁸

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We gratefully acknowledge financial support from the US National Institute of Health (2R01GM50422).

Notes and references

- (a) Solomon EI, Heppner DE, Johnston EM, Ginsbach JW, Cirera J, Qayyum M, Kieber-Emmons MT, Kjaergaard CH, Hadt RG, Tian L. *Chem Rev.* 2014; 114:3659. [PubMed: 24588098] (b) Solomon EI, Sundaram UM, Machonkin TE. *Chem Rev.* 1996; 96:2563. [PubMed: 11848837]
- (a) Allen SE, Walvoord RR, Padilla-Salinas R, Kozlowski MC. *Chem Rev.* 2013; 113:6234. [PubMed: 23786461] (b) Wendlandt AE, Seuss AM, Stahl SS. *Angew Chem Int Ed.* 2011; 50:11062.
- (a) Ghosh S, Cirera J, Vance MA, Ono T, Fujisawa K, Solomon EI. *J Am Chem Soc.* 2008; 130:16262. [PubMed: 18998639] (b) Jazdzewski BA, Holland PL, Pink M, Young VG Jr, Spencer DJE, Tolman WB. *Inorg Chem.* 2001; 40:6097. [PubMed: 11703106] (c) Jazdzewski BA, Tolman WB. *Coord Chem Rev.* 2000; 200–202:633.(d) Bullock JI, Hobson RJ, Povey DC. *J Chem Soc Dalton Trans.* 1974:2037.(e) Calderazzo F, Marchetti F, Dell'Amico G, Pelizzi G, Colliganti A. *J Chem Soc Dalton Trans.* 1980:1419.(f) Kwik W-L. *J Coord Chem.* 1988; 19:279.(g) Whittaker MM, Chuang YY, Whittaker JW. *J Am Chem Soc.* 1993; 115:10029.(h) Ji B, Zhou Z, Ding K, Li Y. *Polyhedron.* 1998; 17:4327.(i) Lyons CT, Stack TDP. *Coord Chem Rev.* 2013; 257:528. [PubMed: 23264696] (j) Fujisawa K, Iwata Y, Kitajima N, Higashimura H, Kubota M, Miyashita Y, Yamada Y, Okamoto K-i, Moro-oka Y. *Chem Lett.* 1999; 28:739.
- (a) Zhang X, Emge TJ, Ghosh R, Krogh-Jespersen K, Goldman AS. *Organometallics.* 2006; 25:1303.(b) Camus A, Marsich N, Nardin G, Randaccio L. *J Chem Soc Dalton Trans.* 1975:2560.(c) Marsich N, Camus A. *J Inorg Nucl Chem.* 1977; 39:275.(d) Cook JA, Drew MGB, Rice DA. *J Chem Soc Dalton Trans.* 1975:1973.(e) Diel BN, Hope H. *Inorg Chem.* 1986; 25:4448.(f) Ito H, Ito T. *Chem Lett.* 1985; 14:1251.(g) Kovacs T, Speier G, Reglier M, Giorgi M, Vertes A, Vanko G. *Chem Commun.* 2000:469.(h) Balogh-Hergovich E, Speier G, Huttner G, Zsolnai L. *Inorg Chem.* 1998; 37:6535. [PubMed: 11670776] (i) Kubota M, Yamamoto A. *Bull Chem Soc Jpn.* 1978; 51:2909.(j) Yamamoto T, Kubota M, Miyashita A, Yamamoto A. *Bull Chem Soc Jpn.* 1978; 51:1835.
- Porter TR, Capitaio D, Kaminsky W, Qian Z, Mayer JM. *Inorg Chem.* 2016; 55:5467. [PubMed: 27171230]
- (b) τ is defined as $\tau = (\beta - \alpha)/60^\circ$ where α and β are the two greatest valence angles of the coordination center and $\beta > \alpha$. Addison AW, Rao TN, Reedijk J, Verschoor GC. *J Chem Soc Dalton Trans.* 1984:1349.
- Lu J-M, Rosokha SV, Neretin IS, Kochi JK. *J Am Chem Soc.* 2006; 128:16708. [PubMed: 17177421]
- Kumar M, Dixon NA, Merkle AC, Zeller M, Lehnert N, Papish ET. *Inorg Chem.* 2012; 51:7004. [PubMed: 22671968]
- Mabbs FE., Collison, D. *Electron Paramagnetic Resonance of d Transition Metal Compounds.* Elsevier Science; Amsterdam: 1992.
- Tolman WB. *Inorg Chem.* 1991; 30:4877.(b) $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-OAc}$ was prepared as described in reference 9a, crystallized from pentane at -30°C and characterized by x-ray crystallography. See Electronic Supporting Information for additional details.
- Vela J, Stoian S, Flaschenriem CJ, Munck E, Holland PL. *J Am Chem Soc.* 2004; 126:4522. [PubMed: 15070362]
- (a) Yoon K, Parkin G. *J Am Chem Soc.* 1991; 113:8414.(b) Han R, Looney A, McNeill K, Parkin G, Rheingold AL, Haggerty BS. *J Inorg Biochem.* 1993; 49:105.(c) Hambley TW, Lynch MJ, Zvargulis ES. *J Chem Soc Dalton Trans.* 1996:4283.

13. Ruggiero CE, Carrier SM, Antholine WE, Whittaker JM, Cramer CJ, Tolman WB. *J Am Chem Soc.* 1993; 115:11285.
14. Carrier SM, Ruggiero CE, Houser RP, Tolman WB. *Inorg Chem.* 1993; 32:4889.
15. Manner VW, Markle TF, Freudenthal JH, Roth JP, Mayer JM. *Chem Commun.* 2008:256.
16. Porter TR, Kaminsky W, Mayer JM. *J Org Chem.* 2014; 79:9451. [PubMed: 25184812]
17. (a) The molar extinction coefficient of TEMPO is reported in dichloromethane and taken to be the same in benzene here Wu A, Mader EA, Datta A, Hrovat DA, Borden WT, Mayer JM. *J Am Chem Soc.* 2009; 131:11985. [PubMed: 19618933]
18. (a) $\text{BDFE}(\text{O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O}-\text{H}) = 80.4 \text{ kcal mol}^{-1}$ ¹² and $\text{BDFE}(\text{}^t\text{Bu}_3\text{ArO}-\text{H}) = 76.7 \text{ kcal mol}^{-1}$. ¹⁴ (b) Warren JJ, Tronic TA, Mayer JM. *Chem Rev.* 2010; 110:6961. [PubMed: 20925411]
19. Warren JJ, Mayer JM. *Proc Natl Acad Sci.* 2010; 107:5282. [PubMed: 20215463]
20. Cook C, Gilmour N. *J Org Chem.* 1960; 25:1429.
21. Costentin C, Evans DH, Robert M, Saveant J-M, Signh PS. *J Am Chem Soc.* 2005; 127:12490. [PubMed: 16144387]
22. Waidmann CR, Miller AJM, Ng C-WA, Scheuermann ML, Porter TR, Tronic TA, Mayer JM. *Energy Environ Sci.* 2012; 5:7771.
23. Hayes EC, Porter TR, Barrows CJ, Kaminsky W, Mayer JM, Stoll S. *J Am Chem Soc.* 2016; 138:4132. [PubMed: 26907976]
24. Looney A, Han R, Gorrell IB, Cornebise M, Yoon K, Parkin G, Rheingold AL. *Organometallics.* 1995; 14:274.
25. Cross GG, Fischer A, Henderson GN. *Can J Chem.* 1984; 62:2803.
26. Mader EA, Davidson ER, Mayer JM. *J Am Chem Soc.* 2007; 129:5153. [PubMed: 17402735]
27. Stoll S, Schweiger A. *J Magn Reson.* 2006; 178:42. [PubMed: 16188474]
28. (a) Schulz S, Roesky HW, Noltemeyer M, Schmidt H-G. *J Chem Soc Dalton Trans.* 1995:177. (b) Cetinkaya B, Gumrukcu I, Lappert MF, Atwood JL, Shakir R. *J Am Chem Soc.* 1980; 102:2086.

Figure 1. ORTEP representations of $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}(\kappa^2\text{-O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O})$ (**1**), $\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}(\kappa^1\text{-O}_2\text{N}^t\text{Bu}_2\text{C}_6\text{H}_2\text{O})$ (**2**) and $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-OC}_6\text{H}_4\text{NO}_2$ (**3**) showing 50% probability thermal ellipsoids and select atom labels. Hydrogen atoms are omitted for clarity.

Figure 2. X-Band EPR Spectra of (1) (top) and (3) (bottom) in toluene glasses at 120 K. Data are shown in black and simulations are shown in red.

Figure 3. Schematic of the reaction between 2.5 mM $[\text{Tp}^{\text{tBu}}\text{Cu}^{\text{I}}]_2$, 2 equivalents of $\text{O}_2\text{N}^{\text{tBu}}\text{C}_6\text{H}_2\text{O}-\text{H}$ and two equivalents of $^{\text{tBu}}\text{ArO}^\bullet$ in benzene and the optical traces of the reaction carried out over the course of 1 hour. The blue arrow shows the disappearance of $^{\text{tBu}}\text{ArO}^\bullet$ with time while the green arrow shows the appearance of **1**.

Scheme 1.

A. Phenolate and nitronato-quinone resonance forms of $t\text{Bu}_2\text{-NO}_2\text{-ArO}^-$. **B.** α -Deprotonation of aliphatic nitro compounds.

Table 1Select Bond Distances (in Å) of Nitrophenol-Derived Ligands in Complexes **1**, **2** and **3**.

	$\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}(\kappa^2\text{-O}_2\text{N}^i\text{Bu}_2\text{C}_6\text{H}_2\text{O})$ (1)	$\text{Tp}^{\text{tBu}}\text{Zn}^{\text{II}}(\kappa^1\text{-O}_2\text{N}^i\text{Bu}_2\text{C}_6\text{H}_2\text{O})$ (2)	$\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}(\text{OC}_6\text{H}_4\text{NO}_2)$ (3)
O2-N7	1.307(5)	1.3314(13)	1.232(3)
O3-N7	1.293(5)	1.2660(14)	1.221(3)
N7-C22	1.333(6)	1.3441(16)	1.449(3)
C22-C23	1.420(7)	1.4270(17)	1.390(3)
C23-C24	1.360(6)	1.3505(18)	1.379(3)
C24-C25	1.486(7)	1.4854(17)	1.410(3)
C25-C26	1.476(8)	1.4900(17)	1.406(3)
C26-C27	1.355(7)	1.3549(17)	1.371(3)
C27-C22	1.434(7)	1.4287(17)	1.392(3)
C25-O1	1.236(7)	1.2338(16)	1.324(3)