

Spectroscopic and kinetic studies of the reaction of $[\text{Cu}^{\text{I}}(6\text{-PhTPA})]^+$ with O_2

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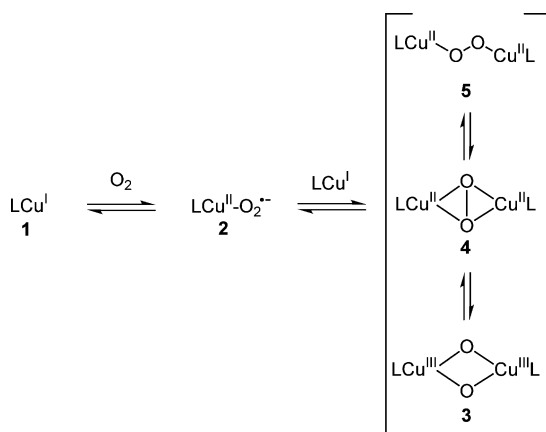
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Oxygenation of $[\text{Cu}^{\text{I}}(6\text{-PhTPA})](\text{SbF}_6)$ in acetone at $-90\text{ }^\circ\text{C}$ produces a short-lived $\text{Cu}^{\text{III}}(\mu\text{-O})_2$ intermediate that exhibits an oxygen-isotope-sensitive $\nu_{\text{Cu-O}}$ mode at 599 cm^{-1} and an overtone at 1192 cm^{-1} . The formation of this intermediate is very fast and is second-order in copper(I) complex, implying that two copper-containing species interact in the rate-limiting step or in pre-equilibrium steps prior to the rate determining step. The decay of this intermediate was facile even at $-90\text{ }^\circ\text{C}$ but did not afford any arene hydroxylation product. Interestingly, the effect of introducing a 6-phenyl substituent on the TPA ligand framework differs from that of a 6-methyl substituent, providing access to a bis(μ -oxo)dicopper(III) intermediate in the former and a (μ -1,2-peroxo)dicopper(II) species in the latter.

Introduction

The reactions of synthetic $\text{Cu}^{\text{I}}(\text{L})$ complexes with O_2 have been vigorously explored as models for copper oxygenases,^{1,2} leading to the trapping of a variety of copper–dioxygen adducts at low temperatures (Scheme 1). Prototypical examples include an end-on bound (μ -1,2-peroxo)dicopper(II) complex,³ a side-on (μ - η^2 : η^2 -peroxo)dicopper(II) complex,⁴ and a bis(μ -oxo)dicopper(III) complex.⁵ Which adduct is observed depends on the nature of the supporting ligand and/or reaction conditions (*i.e.* solvent). In general, tetradentate ligands favor (μ -1,2-peroxo)dicopper(II) adducts, facial tridentate ligands favor (μ - η^2 : η^2 -peroxo)dicopper(II) complexes, and bidentate ligands favor bis(μ -oxo)dicopper(III) complexes. In some cases, rapid interconversion between the two forms is observed.^{1,2,6}



Scheme 1

One structural feature that controls the (μ -peroxo)dicopper(II)/bis(μ -oxo)dicopper(III) equilibrium is the steric bulk of the sup-

porting ligands. This is particularly well illustrated by copper complexes of the tris(2-pyridylmethyl)amine (TPA) family of ligands. While complexes of the parent TPA ligand and its 4-substituted derivatives invariably produce (μ -1,2-peroxo)dicopper(II) species upon oxygenation,^{3,7} the more sterically hindered copper(I) complex $[\text{Cu}(6\text{-Me}_2\text{TPA})]^+$ gives rise to a crystallographically characterized bis(μ -oxo)dicopper(III) complex.⁸ This structure shows the significant lengthening of the axial Cu–N bonds that arise from the two 6-methylpyridine ligands, making 6-Me₂TPA effectively almost a bidentate ligand. Interestingly, when only a single 6-methyl substituent is introduced on one pyridine arm of TPA, the steric hindrance appears not to be significant enough to promote formation of a bis(μ -oxo)dicopper(III) species, and a μ -1,2-peroxo intermediate was observed instead upon exposure of $[\text{Cu}(6\text{-MeTPA})]^+$ to dioxygen.^{9,10} We now demonstrate that replacing the 6-methyl group with a larger phenyl group allows for exclusive formation of a dicopper(III) species from a copper(I) complex with the singly substituted 6-PhTPA ligand.

Experimental

General experimental protocols were described previously, including the syntheses of $[\text{Cu}(\text{NCCH}_3)_4](\text{SbF}_6)$ ¹¹ and the 6-Ph-TPA and 6-Ph-*d*₅-TPA ligands.¹² The 6-Ph-TPA-*d*₆ ligand was obtained following the procedure of Szajna *et al.*¹³ Solutions of copper(I) salts and complexes were handled under inert atmosphere in a glove box. Acetone was refluxed over KMnO_4 , dried over activated 4 Å sieves, and distilled before use.

Preparation of $[\text{Cu}^{\text{I}}(6\text{-PhTPA})](\text{SbF}_6) \cdot \text{THF}$ (1- SbF_6)

THF solutions (4 mL) of 6-PhTPA (159 mg, 0.43 mmol) and $[\text{Cu}(\text{NCCH}_3)_4](\text{SbF}_6)$ (201 mg, 0.43 mmol) were separately prepared under N_2 . The ligand solution was added dropwise to the copper(I) salt solution, and the resulting bright yellow solution was carefully layered with 12 mL hexane. Yellow crystals formed on standing for 48 h. The mother-liquor was decanted and the crystals were washed with hexane and dried to constant mass. Yield 278 mg (0.37 mmol, 87%). Anal. Calc. (Found) for $\text{C}_{28}\text{H}_{30}\text{CuF}_6\text{N}_4\text{OSb}$: C, 45.58 (46.06); H, 4.10 (4.13); F, 15.45 (15.32); N, 7.59 (7.71)%. ¹H NMR (*d*₆-acetone, 293 K, δ in ppm): 8.53 (2H, α); 8.47 (2H,

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o); 8.03 (1H, γ); 7.90 (3H, β' and γ); 7.81 (2H, m); 7.71 (1 H, p); 7.52 (3H, β' and β remote from α); 7.45 (2H, β); 4.44 (2H); 4.38 (4H).

X-Ray crystal structure determination for $[\text{Cu}^{\text{I}}(6\text{-PhTPA})_2](\text{PF}_6)_2 \cdot 2\text{THF} (1\text{-PF}_6)$

The sample was prepared starting from $[\text{Cu}(\text{NCCH}_3)_4](\text{PF}_6)$ and 6-PhTPA as described for the corresponding SbF_6 salt above. A suitable crystal (dimensions $0.36 \times 0.18 \times 0.08$ mm) was placed on a glass capillary. Data was collected on a Bruker SMART diffractometer at 173(2) K using graphite-monochromated Mo-K α radiation. Absorption corrections were performed using the SADABS program.¹⁴ The SAINT program was used to integrate the intensity data.¹⁵ The structure was solved by direct methods using SHELXS-86 and refined using SHELXL-97.¹⁶ All non-hydrogen atoms were refined anisotropically except those of one PF_6^- ion and both THF molecules. All hydrogen atoms were placed in ideal positions and refined as riding atoms except for those on the disordered THF molecules. These were excluded from the refinement but included in the calculation of global parameters. The data collection is summarized in Table 1.

CCDC reference number 258073.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603285k

Stopped-flow kinetic measurements

These experiments were performed using a Hi-Tech Scientific (Salisbury, Wiltshire, UK) SF-43 multi-mixing anaerobic cryogenic stopped-flow instrument combined with either a monochromator or a diode array rapid scanning unit. Saturated solutions of O_2 in acetone were prepared by bubbling the dry O_2 gas for 15 min through argon-saturated acetone in a gas-tight syringe at room temperature. The solutions of a copper(I) complex and O_2 were cooled to a preset temperature in the stopped-flow instrument before mixing. For the kinetic experiments, dioxygen was always taken in large excess so that its concentration does not change significantly during the reaction. Data analysis was performed with the IS-2 Rapid Kinetics Software (Hi-Tech Scientific) for kinetic traces at a single wavelength, or with the Specfit program

Table 1 Summary of the X-ray data collection for $[\text{Cu}^{\text{I}}(6\text{-PhTPA})_2](\text{PF}_6)_2 \cdot 2\text{THF} (1\text{-PF}_6)$

Formula	$\text{C}_{36}\text{H}_{35}\text{Cu}_2\text{F}_{12}\text{N}_8\text{O}_2\text{P}_2$
M_r	1289.10
Crystal system	Triclinic
Space group	$P\bar{1}$
Z	2
$a/\text{\AA}$	10.731(3)
$b/\text{\AA}$	11.893(3)
$c/\text{\AA}$	23.132(6)
$\alpha/^\circ$	93.038(4)
$\beta/^\circ$	100.387(4)
$\gamma/^\circ$	102.307(4)
$V/\text{\AA}^3$	2824.2(13)
T/K	173(2)
$\lambda(\text{Mo-K}\alpha)/\text{\AA}$	0.71073
$R1 (I > 2\sigma(I))$	0.0621
$wR2 (I > 2\sigma(I))$	0.1552

(BioLogic Science Instruments, Grenoble, France) for global fitting of the spectral changes acquired in a diode-array mode. The details of similar stopped-flow experiments were described elsewhere.¹⁷

Results and discussion

Our interest in bio-inspired, metal-catalyzed arene hydroxylation led us to investigate the coordination chemistry of the 6-PhTPA ligand, previously reported by Canary.¹⁸ The iron(II) complex of 6-PhTPA reacts with oxidants to form an oxoiron(IV) intermediate that affords hydroxylation of the phenyl ring.¹² The corresponding copper(I) complex salts $[\text{Cu}^{\text{I}}(6\text{-PhTPA})(\text{EF}_6)] \cdot \text{THF}$ ($E = \text{P}, \text{Sb}$) complexes, designated **1-PF₆** and **1-SbF₆**, were obtained as yellow crystals in good yields. X-Ray crystallography revealed a dimeric structure for **1-PF₆**, with one of the two pyridylmethyl arms of the tetradentate 6-PhTPA ligand bridged to the second copper(I) cation (Fig. 1). This bridging mode has been proposed for other copper(I) complexes of tetradentate tripodal ligands⁷ and established for $[\text{Cu}^{\text{I}}_2(\text{BPiA})_2](\text{OTf})_2$ ¹⁹ and copper(I) complexes of some scorpionate ligands.^{20,21}

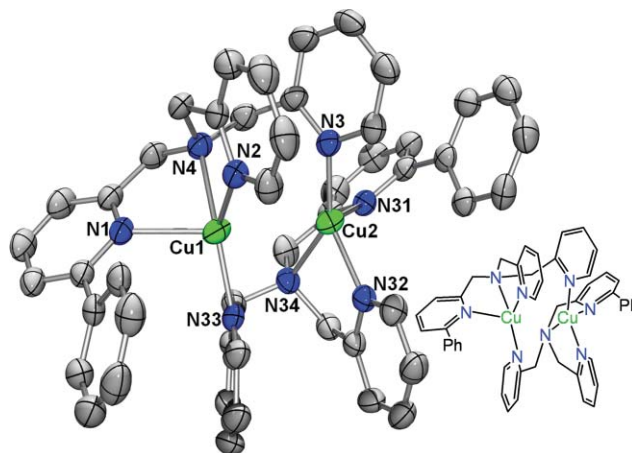


Fig. 1 ORTEP plot of the dimeric complex dication of **1-PF₆**. Ellipsoids are drawn at 50% probability level for clarity. Coordination bond lengths (\AA): Cu1–N1 2.264(4), Cu1–N2 2.048(5), Cu1–N4 2.196(4), Cu1–N33 1.966(4), Cu2–N31 2.233(4), Cu2–N32 2.037(5), Cu2–N34 2.240(4), Cu2–N3 1.958(4). Bottom right: ChemDraw representation of the structure.

In contrast, solution-phase ^1H NMR spectra of **1-SbF₆** in d_6 -acetone recorded at room temperature were indicative of mirror plane symmetry, consistent with dissociation to a monomeric structure. Although the compound was indefinitely stable in this solution under inert atmosphere, exposure to O_2 at room temperature resulted in immediate conversion to a pale blue solution of a simple tetragonal copper(II) complex, as judged by the appearance of typical ligand field bands above 600 nm.²² In contrast, oxygenation in acetone at -65 to -90 $^\circ\text{C}$ resulted in rapid development of a bright yellow color, coincident with the appearance of a metastable chromophore with λ_{max} at 378 nm (Fig. 2). These spectral changes are characteristic of the formation of an intermediate with a bis(μ -oxo)dicopper(III) core.¹

Formulation of the intermediate obtained from $[\text{Cu}(6\text{-PhTPA})]^+$ and O_2 as a bis(μ -oxo)dicopper(III) complex is supported by

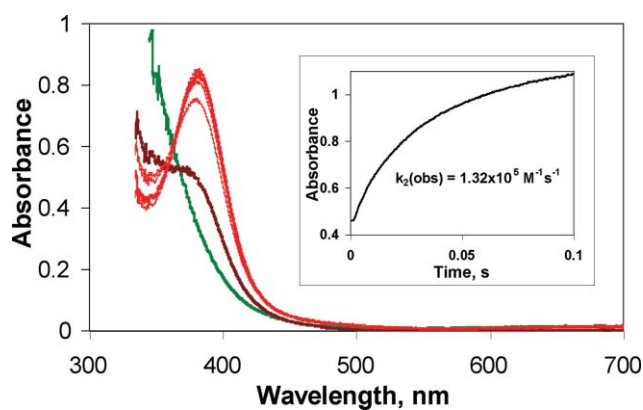


Fig. 2 Spectral changes observed upon mixing of acetone solutions of $[\text{Cu}(6\text{-PhTPA})]^+$ with excess oxygen in the stopped-flow spectrophotometer at -65°C : formation of **3**. Concentrations of solution: $[\text{Cu}(6\text{-PhTPA})]^+$, 0.25 mM; O_2 , 4 mM. Green: spectrum of $[\text{Cu}(6\text{-PhTPA})]^+$; brown: spectrum of the reaction mixture immediately after mixing (within *ca.* 2 ms mixing time); red: accumulation of **3** over 1 s. Inset: single-wavelength registration (at 380 nm) of the formation of **3** overlaid with a second-order fit.

resonance-Raman data obtained from a frozen aliquot of reaction solution using 406.7-nm excitation. The obtained spectrum was dominated by an intense resonance-enhanced mode at 599 cm^{-1} that shifted to 573 cm^{-1} when $^{18}\text{O}_2$ was used to generate the sample (Fig. 3), consistent with assignment to a $\nu(\text{Cu}-\text{O})$ mode. Use of 50% ^{18}O -enriched O_2 gas as mixed isotopomers produced a third band at 592 cm^{-1} . These spectral features are associated with the formation of a $\text{Cu}^{\text{III}}_2(\mu\text{-O})_2$ core.^{23,24} Similar Raman spectra were reported for complexes of related 6-substituted TPA ligands 6-Me₂-TPA and 6-Me₃-TPA.⁸

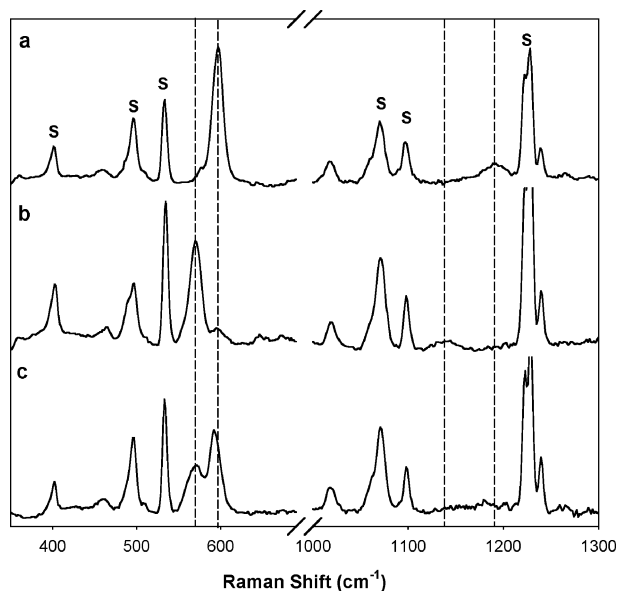


Fig. 3 Resonance-Raman spectra of oxygenated **1-SbF₆** recorded using 406.7-nm radiation: (a) with $^{16}\text{O}_2$, (b) with $^{18}\text{O}_2$, (c) with 25% $^{16}\text{O}_2$, 50% $^{16}\text{O}^{18}\text{O}$ and 25% $^{18}\text{O}_2$. Acetone peaks are labeled 's'.

Further scrutiny of the Raman spectrum of the intermediate derived from **1** reveals a second, less strongly enhanced band at 1192 cm^{-1} (Fig. 3). The fact that this frequency is nearly double

that of the intense 599 cm^{-1} mode and exhibits an ^{18}O downshift of 52 cm^{-1} supports its assignment as the overtone of the $\nu(\text{Cu}-\text{O})$ mode. Despite the wealth of vibrational information available on copper-dioxygen adducts,^{23,24} the only other report of such an overtone feature has been made by Stack, Solomon and co-workers on a complex with the *N,N'*-dimethyl-*N,N'*-diethyl-*trans*-1,2-diaminocyclohexane ligand.²³ The Raman data thus establish that **1** reacts with O_2 to form an intermediate with a $\text{Cu}^{\text{III}}_2(\mu\text{-O})_2$ core.

The reaction between complex **1** and dioxygen in acetone was monitored by stopped-flow spectrophotometry at low temperatures (from -80 to -50°C). Spectral changes observed in the stopped-flow experiments agreed well with UV-Vis spectral changes recorded at -90°C by conventional benchtop spectrophotometry. Immediately upon mixing of **1** with O_2 , an intense absorption band with $\lambda_{\text{max}} = 378\text{ nm}$ began to grow (Fig. 2), which corresponds to the bis(μ -oxo)dicopper(III) intermediate **3**. The reaction proved to be very fast; formation of **3** was complete in *ca.* 0.1 s under most of the reaction conditions used in our experiments (0.25 mM solutions of **1**, 1–4 mM solutions of O_2 after mixing in the stopped-flow cell). Only one observable kinetic step was found on a millisecond to second time scale (Fig. 2, inset), and there was no apparent accumulation of a (μ -peroxo)dicopper(II) species that may be evidenced by distinctive absorption features in the 500–600-nm region like those observed for (μ -1,2-peroxo)dicopper(II) TPA complexes.^{3,7} If a peroxo species is formed in this reaction, its concentration must be very low, presumably due to its rapid conversion into dicopper(III) intermediate **3**. Another putative intermediate in the oxygenation of **1**, a superoxo complex **2**, would be expected to have an absorption spectrum with $\lambda_{\text{max}} \sim 420\text{ nm}$.^{7,25} While such an absorption band of the superoxo intermediate would be well separated from features of a dicopper(II) peroxo complexes, thus allowing for an unambiguous registration of the superoxo species for a series of 4-substituted TPA ligands, it would overlap significantly with the absorption band of bis(μ -oxo)dicopper(III) complex **3** that forms in our system. It is therefore difficult to observe the superoxo intermediate (*e.g.*, **2**) in our stopped-flow spectrophotometric experiments. Additionally, formation of the copper(II)-superoxo species from Cu(I) and O_2 in non-coordinating solvents was previously reported to be very fast, exceeding the stopped-flow timescale in Cu(I)-TPA systems ($k = 1.5 \times 10^8\text{ M}^{-1}\text{ s}^{-1}$ for Cu(TPA) in THF determined by flash photolysis).²⁶ However, the first spectrum observed immediately after mixing acetone solutions of **1** and O_2 (mixing time: *ca.* 2 ms) is different from the spectrum of the starting complex **1** and is also different from the extrapolation of the spectrum of **3** to time 0 (or to 2 ms). This observation suggests that a superoxo intermediate may indeed be rapidly accumulated in the first pre-equilibrium step of oxygen binding to **1**; however, the rapid absorption change may also reflect other pre-equilibrium processes at low temperature. Clearly, additional experiments at temperatures below -80°C would be required to unambiguously detect the superoxo complex.

The observed kinetic step for oxygenation of **1**, resulting in the formation of **3**, is second-order in copper(I) complex (Fig. 2, inset). This conclusion follows from the following experimental observations: (i) under a large excess of oxygen (at least 10-fold with respect to complex **1**), the kinetic traces cannot be fit to a single-exponential equation typical of a process with first-order dependence on **1**, but can be fit nearly perfectly to

a second-order rate law; (ii) the observed reaction rates depend on the concentration of **1**, while second-order rate constants do not. The second order dependence on **1** implies that two copper-containing species interact in the rate-limiting step or in pre-equilibrium steps prior to the rate determining step. For example, a similar second-order dependence in copper(I) complex has been reported for the formation of (μ -1,2-peroxo)dicopper(II) intermediates from copper(I) complexes of TPA-type ligands⁷ and of bis(μ -oxo)dicopper(III) intermediates from copper(I) complexes with derivatives of di(pyridylethyl)amine.²⁷ This was interpreted in terms of a rate-limiting interaction between a rapidly formed copper(II)-superoxo intermediate and a second molecule of Cu(I)L, followed by a rapid conversion of the unobserved (μ -peroxo)dicopper(II) complex intermediate into the product bis(μ -oxo)dicopper(III) species. An alternative interpretation is also possible, involving dimerization of the copper(I) complex prior to its reaction with O₂, followed by another bimolecular reaction to form a tetranuclear copper(II)-peroxo intermediate, which eventually yields a dinuclear copper(II) peroxo species.⁷ This rather complicated reaction scheme was established by Karlin, Zuberbühler and co-workers for the oxygenation of copper(I) complexes with 4-substituted TPA in acetone.⁷ Although it was possible to determine all individual kinetic parameters for the 4-^tBu₃TPA, a series of related complexes gave rise to an even more complicated oxygenation, where experimental data could not be easily explained by a particular kinetic model.⁷ Unfortunately, we were also unable to completely model oxygenation kinetics of **1**, or determine individual rate constants and activation parameters. A multistep mechanism for this reaction is confirmed by the unusual negative activation energy observed for the second-order oxygenation of **1** ($E_a = -4.6$ kcal mol⁻¹, Fig. 4). This observation requires that an unobserved exothermic pre-equilibrium step precedes the observed formation of **3**. A similar negative activation energy was reported by Karlin and co-workers in their study of the oxygenation of the copper(I) complex of N-methylated di(aminopropyl)amine.²⁸

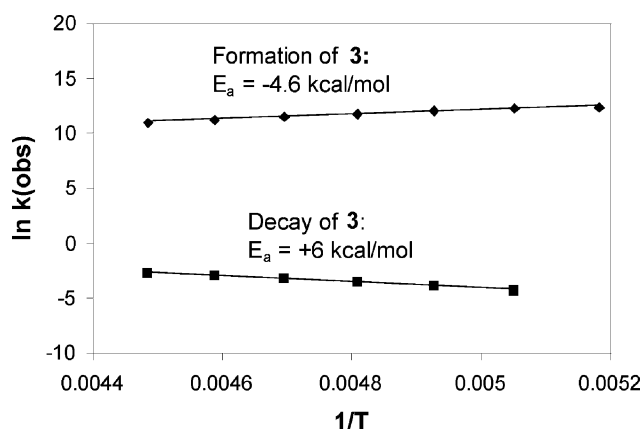


Fig. 4 Arrhenius plots for the reactions of second-order formation of **3** and first-order decay of **3**, measured under concentration conditions listed in Fig. 2.

Complex **3** is surprisingly unstable, decomposing within 20 minutes at -90 °C, in contrast to the 6-Me₂TPA intermediate, which was stable enough to be crystallized.⁸ The decomposition

kinetics of **3** showed a clean, first-order process, characterized by a positive activation energy of 6 kcal mol⁻¹ (Fig. 4 and 5). Analysis of the reaction products upon warming shows that 6-PhTPA was recovered largely intact from decomposed **3**. Electrospray mass spectrometry of the decomposed solution gave ions corresponding to Cu(II) complexes of intact ligand, which were shifted 5 amu higher using the 6-Ph-*d*₅-TPA ligand complex, and 6 amu higher when the ligand methylene carbons were exhaustively substituted with deuterium. These isotopic substitutions appeared not to perturb the formation and decay kinetics of **3**. Consistent with these results, only a trace amount of pyridine 2-carbaldehyde resulting from N-dealkylation of the tertiary amine was detected, unlike the significant ligand oxidation reported for decomposition of Cu^{III}₂(μ -O)₂ complexes of 6-Me₂TPA and 6-Me₃TPA.²⁹ Hydroxylation of the phenyl ring also did not occur, unlike for the Fe(6-PhTPA) complex¹² or a Cu^{III}₂(μ -O)₂ intermediate supported by the closely related bidentate 2-(diethylaminomethyl)-6-phenylpyridine ligand.³⁰ We attribute the lack of phenyl ring hydroxylation on 6-PhTPA to axial displacement of the phenylpyridine arm from the Cu^{III}₂(μ -O)₂ diamond core, similar to that found in the crystal structure of [Cu^{III}(μ -O)₂(6-Me₂TPA)₂]²⁺.⁸ This bond elongation or dissociation would preclude a favorable geometry for oxo-atom transfer from the Cu₂O₂ core to the pendant phenyl group.

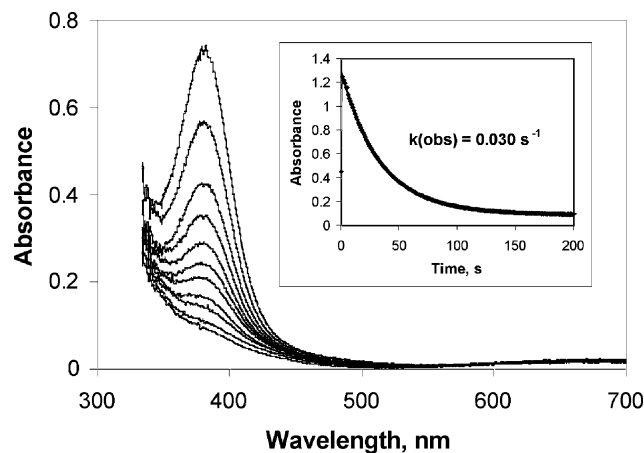


Fig. 5 Decomposition of **3** observed by stopped-flow spectrophotometry over 400 s at -65 °C. Reaction conditions are the same as those in Fig. 2. Inset: Single-wavelength registration (at 380 nm) of the decay of **3** overlaid with a first-order fit.

Conclusions

In summary, we have reported the reaction of the copper(I) complex of a 6-phenyl substituted TPA ligand with O₂ at -90 °C in acetone forms a short-lived intermediate with a Cu^{III}₂(μ -O)₂ core. The presence of this core is established by its characteristic Raman signature at 599 cm⁻¹ and a rarely observed overtone at 1192 cm⁻¹. This result differs from that of [Cu^I(6-MeTPA)]⁺, which affords a (μ -1,2-peroxo)dicopper(II) intermediate upon exposure to O₂, presumably due to the difference in the sizes of the 6-substituents. Interestingly, decay of the [Cu^{III}₂(μ -O)₂(6-PhTPA)₂]²⁺ intermediate does not result in the hydroxylation of the appended phenyl ring.

Abbreviations

TPA, tris(2-pyridylmethyl)amine; $\text{Tp}^{\text{Bu},\text{iPr}}$, hydrotris(3-*tert*-butyl-5-isopropylpyrazolyl)borate anion; Me_6tren , tris(dimethylaminoethyl)amine; TMG_3tren , tris(tetramethylguanidinoaminoethyl)amine; 6-PhTPA, (6-phenyl-2-pyridylmethyl)bis(2-pyridylmethyl)amine; BPIA, bis(2-pyridylmethyl)(1-methylimidazol-2-ylmethyl)amine; 6-MeTPA, (6-methyl-2-pyridylmethyl)bis(2-pyridylmethyl)amine; 6-Me₂TPA, (2-pyridylmethyl)bis(6-methyl-2-pyridylmethyl)amine; 6-Me₃TPA, tris(6-methyl-2-pyridylmethyl)amine.

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