Mononuclear Copper(II)−Acylperoxo Complexes

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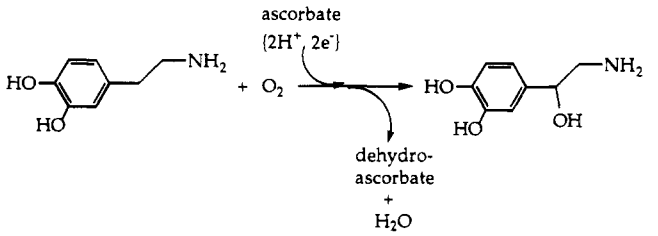
Peroxocopper complexes are of interest in metal ion mediated oxidative processes and as potential models for the active-site chemistry of copper metalloproteins involved in dioxygen (O_2) processing. Having been implicated in certain copper monooxygenases, mononuclear Cu(II)−OOR species are of particular interest. Here, the generation, spectroscopic characterization, and reactivity with triphenylphosphine of three mononuclear acylperoxo−copper(II) complexes are described. $[Cu(TMPA)(m\text{-}ClC_6H_4C(O)OO^-)]^+$ (**1**; TMPA = tris(2-pyridylmethyl)-amine) was formed by low-temperature reaction of the peroxo−dicopper(II) species $[\{Cu^{II}(TMPA)\}_2(O_2^{2-})]^{2+}$ (**5**) with *m*-chloroperoxybenzoic acid (*m*-CPBA); hydrogen peroxide is a byproduct in this acid−base reaction. A trigonal-bipyramidal mononuclear coordination in **1** is supported by UV−vis and EPR evidence, while a 1740 cm^{-1} carbonyl infrared absorption suggests the percarboxylato ligand binds as a unidentate oxygen donor ligand. Reaction of **1** with PPh_3 at −80 °C gives $O{=}PPh_3$ and the carboxylato complex $[Cu(TMPA)(m\text{-}ClC_6H_4C(O)O^-)]^+$ (**6**) ($\nu_{C=O}$ = 1620 cm^{-1}). $[Cu(Me_2im)_3(m\text{-}ClC_6H_4C(O)OO^-)]^+$ (**2**; Me_2im = 1,2-dimethylimidazole) is formed by reaction of *m*-CPBA with the peroxo−dicopper(II) species $[Cu_2(Me_2im)_6(O_2)]^{2+}$ (**8**) in CH_2Cl_2 at −90 °C. Solution and solid-state spectroscopic data are consistent with a mononuclear formulation while $\nu_{C=O}$ = 1745 cm^{-1} also suggests terminal percarboxylato coordination. While **1** and **2** are stable at room temperature as solids, $[Cu^{II}(CPY2\text{-}O^-)(m\text{-}ClC_6H_4C(O)OO^-)]$ (**3**; CPY2-OH = bis[2-(2-pyridyl)ethyl][(2-hydroxyphenyl)methyl]-amine) is not. Is was generated by reaction of $[Cu(CPY2\text{-}O^-)(Cl)]\cdot 2H_2O$ (**9**) with *m*-CPBA at −75 °C. At this temperature, a 1750 cm^{-1} IR absorption is ascribable to a coordinated perbenzoato ligand. Species **3** is the most reactive of the three Cu(II)−percarboxylato complexes. Addition of PPh_3 (−80 °C) causes a rapid change, giving $O{=}PPh_3$ and the carboxylato complex $[Cu(CPY2\text{-}O^-)(m\text{-}ClC_6H_4C(O)O^-)]$ (**10**), which was independently synthesized. Percarboxylato complexes **1** and **2** possess enhanced reactivity relative to peroxo−copper(II) complexes with the same ligands, a further example illustrating how electrophilic activation (e.g. by protonation or, here, by acylation) of peroxo groups leads to oxygen atom transfer functionality.

Introduction

In addition to their involvement in chemical oxidative processes,[1,2] peroxo−copper(II) complexes are of interest in bioinorganic chemistry due to their involvement in the processing of dioxygen (O_2) by a variety of copper-containing metalloproteins.[3−6] A variety of functions include reversible dioxygen binding in hemocyanins,[7,8] O_2 activation in copper monooxygenases,[4−6,9,10] and O_2 reduction to water in copper[9,11,12] and heme−copper[13−15] oxidases. Here we describe the synthesis and characterization of mononuclear perbenzoato species $[Cu^{II}(L)(OOR)]^{n+}$ (R = $m\text{-}ClC_6H_4C(O)$−), or *m*-CPBA complexes. Such compounds may be potentially relevant to the chemistry occurring at the active site of the copper-containing monooxygenase dopamine β-hydroxylase (DβH), which catalyzes the ascorbate-dependent stereospecific benzylic hydroxylation of phenylethylamines such as dopamine to the neurotransmitter norepinephrine.[16−18]



The active site of DβH contains two inequivalent Cu(II) ions which do not electronically or magnetically interact; apparently,

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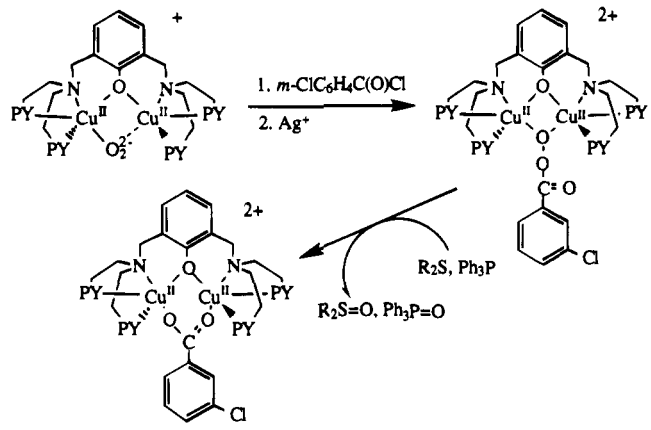
one acts as the electron transfer center, whereas the other copper site effects the hydroxylation.[19] The suggested mechanism involves the fully reduced enyzme initially binding substrate and O_2; electron transfer from the second Cu(I) ion yields a mononuclear copper−hydroperoxide (Cu^{II}−OOH) species, where the proton is supplied by an active-site protein group. The hydroperoxide complex is responsible for the oxygen atom transfer to the substrate (i.e., involving an O−O bond cleavage process). It has been suggested that an active-site tyrosine residue participates in reductive activation of the Cu^{II}−OOH intermediate, to give a more reactive Cu−O• species, which can abstract H• from the substrate; Cu−O rebound leads to the product.[18]

A structurally and catalytically related enzyme is the bifunctional peptidylglycine α-amidating enzyme, for which the peptidyl α-hydroxylating monooxygenase PHM function effects a methylene hydroxylation and N-dealkylation reaction.[20−22] Although speculative at this time, Cu−OOH chemistry could also be involved here. In the "blue" multicopper oxidases (i.e., laccase, ascorbate oxidase) which reduce O_2 to water while effecting one-electron oxidations of a variety of substrates, Solomon and co-workers have detected Cu_2−hydroperoxo intermediates.[9,23]

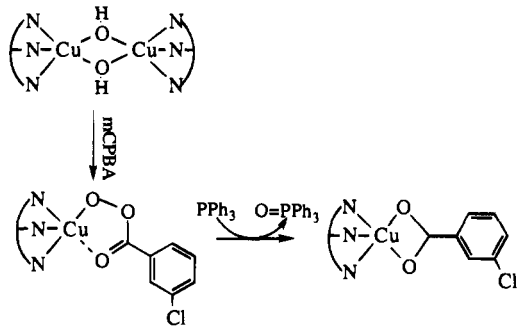
Our own research program has emphasized Cu^I_n/O_2 reactivity, leading to a variety of well-characterized reversible O_2-binding systems,[4,6,24] and monooxygenase model systems involving aromatic hydroxylation.[3,6,10,25] In explorations of peroxo−copper(II) chemistry using dinuclear phenoxo-bridged compounds, we previously described hydroperoxo- and acylperoxo-bridged dicopper(II) complexes $[Cu_2(XYL\text{-}O^-)(OOR)]^{2+}$ (R = H, *m*-$ClC_6H_4C(O)$).[26,27] The acylperoxo complex was characterized by X-ray crystallography, showing a μ-1,1-peroxybenzoato bridge between the two copper(II) ions, while indirect methods indicated a similar coordination for the hydroperoxo complex $[Cu_2(XYL\text{-}O^-)(OOH)]^{2+}$ and a closely related analogue $[Cu_2(UN\text{-}O^-)(OOH)]^{2+}$.[28] These compounds can be generated by the reaction of the appropriate electrophile (i.e., *m*-$ClC_6H_4C(O)Cl$ or H^+, respectively) with their peroxo−dicopper(II) precursor (Scheme 1).[26] The acylperoxo dicopper(II) complexes quantitatively transfer an oxygen atom to simple substrates such as triphenylphosphine and dialkyl sulfides (Scheme 1).

The only mononuclear Cu(II)−OOR complexes thus far isolated and characterized are those due to Kitajima and co-workers. The complex $[Cu(HB(3,5\text{-}i\text{Pr}_2pz)_3)(m\text{-}ClC_6H_4C(O)OO^-)]$ was prepared from a dihydroxo-bridged dicopper(II) precursor, and it reacts with PPh_3 to yield $O{=}PPh_3$ and a Cu(II)−carboxylate complex (Scheme 2). Infrared spectroscopy was used to indicate that the carbonyl oxygen atom on the *m*-CPBA (*m*-chloroperoxybenzoate) group interacts with the copper(II) ion as shown in Scheme 2.[29] By reaction of the same precursor with cumyl hydroperoxide, the alkylperoxo complex $[Cu(HB(3,5\text{-}i\text{Pr}_2pz)_3)(OOCMe_2Ph)]$ was isolated and structurally characterized.[30]

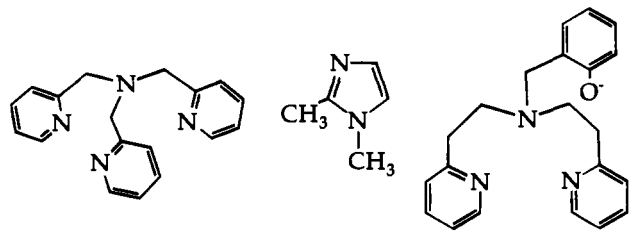
Scheme 1



Scheme 2



With a variety of ligand types in hand for which copper(I)−dioxygen chemistry has been feasible, we sought to generate newer types of mononuclear Cu^{II}−OOR species, so as to explore their chemistry. In this paper, the ligands used for generating copper−acylperoxo complexes $[Cu^{II}(L)(OOC(O)R)]^{n+}$ (R = *m*-ClC_6H_4−; *n* = 0, 1) are TMPA, tris(1,2-dimethylimidazole) (Me_2im) and CPY2-O^-:



TMPA **Me_2im** **CPY2-O^-**

$[Cu^{II}(L)(m\text{-}ClC_6H_4C(O)OO\text{-})]^{n+}$

L = TMPA, **(1)**

L = $(Me_2im)_3$, **(2)**

L = CPY2-O^-, **(3)**

Two of these complexes, $[Cu(TMPA)(m\text{-}ClC_6H_4C(O)OO^-)]^+$

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(**1**) and $[Cu(Me_2im)_3(m\text{-}ClC_6H_4C(O)OO^-)]^+$ (**2**), are stable as solids at room temperature, while the third, $[Cu(CPY2\text{-}O^-)(m\text{-}ClC_6H_4C(O)OO^-)]^+$ (**3**), cannot be isolated due to its thermal sensitivity; however it was generated and characterized at low temperature in solution. The reactivity of these compounds with triphenylphosphine was used to prove the peroxidic nature of these complexes, and these reactions are also described.

Experimental Section

Materials and Methods. Reagents and solvents used were of commercially available reagent grade quality and were purified according to the published procedures.[31] Copper(I) precursors $[Cu(TMPA)(CH_3CN)](PF_6)$ (**4**)[31] and $[Cu(Me_2im)_3](PF_6)$ (**7**)[32] were synthesized according to published procedures. Ligand CPY2-OH and its copper(II) complex $[Cu(CPY2\text{-}O^-)(Cl)]$ (**9**) were also prepared by known methods.[33] Air- and moisture-sensitive compounds were stored and manipulated in a Vacuum Atmospheres drybox filled with Ar. All elemental analyses were performed by Desert Analytics, Tucson, AZ.

Infrared spectra were measured as Nujol mulls on a Perkin-Elmer 710B spectrophotometer using a polystyrene film as calibrant or on a Mattson Galaxy series 4030 FT-IR interfaced with a Compaq Deskpro 386/20e computer. NMR spectra were recorded in CD_3NO_2 on either a Varian EM360 (60-MHz) or a Varian XL-400 (400-MHz) spectrometer. Chemical shifts are reported as δ values downfield from an internal standard Me_4Si. Electrical conductivity of the samples were measured in acetonitrile using a Barnstead Model PM-70CB conductivity bridge and YSI Model 3403 conductivity cell. The cell constant, κ, was determined with a standard aqueous KCl solution. Room-temperature magnetic moments were determined by using a Johnson Matthey magnetic susceptibility balance which was calibrated by using $Hg[Co(SCN)_4]$. X-band electron paramagnetic resonance (EPR) spectra were taken using a Varian E-4 or a Varian E-12 spectrometer in frozen solutions at 77 K with 4 mm o.d. quartz tubes. The field was calibrated with a powder sample of diphenylpicrylhydrazyl (DPPH, g = 2.0037). Solvent used was CH_2Cl_2/toluene (4:1, v/v). The signals obtained were integrated by comparing the intensity observed ($I \approx h_{1/2}(w_{1/2h})^2$) with that of a known concentration of $Cu(NO_3)_2{\cdot}3H_2O$ in MeOH (at 77 K) or with a known solution of $[Cu(tepa)(Cl)](PF_6)$[34] in DMF/$CHCl_3$ (1:1, v/v, 77 K). Room-temperature electronic spectra were recorded with a Shimadzu UV-160 spectrophotometer using quartz cuvettes (1 cm). Low-temperature UV−vis spectra were measured on either a Perkin-Elmer Lambda Array 3840 spectrophotometer driven by an IBM PC or a Hewlett-Packard 8452A diode array spectrophotometer driven by a Compaq Deskpro 386S computer using software written by On-Line Instruments Systems Inc. The spectrophotometer was equipped with a variable-temperature Dewar flask and a cuvette assembly previously described.[31] GC analysis was performed on a Hewlett-Packard HP5890 series gas chromatograph equipped with a capillary injector and a flame ionization detector using a 30 m HP-5 capillary column. Signal integration was obtained by using a HP 3392A integrator.

Synthesis of $[Cu(TMPA)(m\text{-}ClC_6H_4C(O)OO^-)](PF_6){\cdot}0.5CH_2Cl_2$ (1). In a Schlenk flask, CH_2Cl_2 (25 mL) was bubbled with O_2 for 10 min and then was cooled to −90 °C. Solid $[Cu(TMPA)(CH_3CN)](PF_6)$ (**4**) (0.55 g, 1.02 mmol) was added to the solvent under a flow of Ar, forming a purple solution. This was further bubbled with O_2 for 5 min. After the purple solution was stirred for 10 min, excess O_2 was removed by repeated vacuum/Ar applications and *m*-chloroperoxybenzoic acid (0.19 g, 1.11 mmol) was added as a solid. The purple solution slowly became blue over a period of *ca.* 2 h at −90 °C. Once the reaction was over, the reaction mixture was quickly filtered through a coarse frit into a Schlenk flask kept at −90 °C. Under Ar, diethyl ether (300 mL) was added dropwise to the blue solution at −90 °C over a period of ~12 h, resulting in the precipitation of a light blue solid. The ether layer (colorless) was decanted by means of a cannula, and it showed a positive test for H_2O_2 (test paper: Merckoquant 10011, E. Merck). The blue solid was washed with Et_2O (2 × 50 mL) and dried under vacuum at −80 °C. The compound was recrystallized at −90 °C from 30 mL of CH_2Cl_2 and 200 mL of Et_2O to yield 0.43 g (63%) of a blue microcrystalline solid. Anal. Calcd for $C_{25.5}H_{23}Cl_2CuF_6N_4O_3P$: C, 42.95; H, 3.23; N, 7.86. Found: C, 43.02; H, 3.41; N, 7.69. IR (Nujol, cm^{-1}): 1740 (s, C=O), 1605 (s, C=C), 840 (vs, PF_6^-). UV−vis [CH_2Cl_2, −80 °C; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 332 (950), 690 sh (160), 870 (280). Molar conductivity: Λ_M = 154 Ω^{-1} cm^2 mol^{-1}. EPR (CH_2Cl_2/toluene, 77 K): $g_\perp = 2.16$, $A_\perp = 85 \times 10^{-4}$ cm^{-1}. Magnetism (solid state, room temperature): μ_{RT} = 2.00 μ_B/Cu.

KCN Reduction of Complex 1: Confirmation of the Presence of CH_2Cl_2. The presence of dichloromethane in $[Cu(TMPA)(m\text{-}ClC_6H_4C(O)OO)](PF_6){\cdot}0.5CH_2Cl_2$ (**1**) was shown by means of NMR spectroscopy on a chemically reduced sample of the complex. A small quantity of **1** (*ca.* 50 mg) was dissolved in 3 mL of CD_3NO_2, and *ca.* 0.3 g of KCN was added. The mixture was stirred in a tightly sealed tube overnight, resulting in an orange solution with a large amount of precipitate. After stirring, the mixture was allowed to sit for 20 min for the precipitate to settle and the supernatant was transferred to a standard NMR tube. ^1H NMR (CD_3NO_2): δ 3.80 (s, 6 H), 5.35 (s, CH_2Cl_2), 7.10−8.20 (m, 13 H), 8.50 (br, 3 H).

Reaction of $[Cu(TMPA)(m\text{-}ClC_6H_4C(O)OO^-](PF_6){\cdot}0.5CH_2Cl_2$ (1) with PPh_3: Isolation of $[Cu(TMPA)(m\text{-}ClC_6H_4C(O)O^-](PF_6){\cdot}0.5CH_2Cl_2$ (6). A solution of $[Cu(TMPA)(m\text{-}ClC_6H_4C(O)OO)](PF_6){\cdot}0.5CH_2Cl_2$ (**1**) (0.23 g, 0.34 mmol) was prepared in 20 mL of CH_2Cl_2 under Ar at −80 °C. Triphenylphosphine (0.20 g, 0.77 mmol) was added to this solution as a solid, and the mixture was stirred at −80 °C for 4 h. At this stage, an aliquot of the sample was injected into gas chromatographic instrument showing the formation of $O{=}PPh_3$. The mixture was warmed to the room temperature, and Et_2O (100 mL) was added to the solution with formation of a blue precipitate. The diethyl ether layer was decanted and saved, the blue solid was washed thoroughly with Et_2O (2 × 20 mL) and toluene (2 × 10 mL), and the washings were collected together with the previous ether layer. This supernatant was subjected to gas chromatographic analysis, showing a 60:40 PPh_3:$O{=}PPh_3$ mixture (yield of $O{=}PPh_3$ = 80%). The blue solid was dried to give 0.19 g (89%) of product. Anal. Calcd for $C_{25.5}H_{23}Cl_2CuF_6N_4O_2P$: C, 43.93; H, 3.30; N, 8.07. Found: C, 43.79; H, 3.46; N, 8.83. IR (Nujol, cm^{-1}): 1620 (m, C=O), 1605 (s, C=C), 840 (vs, PF_6^-). UV−vis [CH_2Cl_2, −80 °C; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 792 sh (80), 967 (140). Molar conductivity: Λ_M = 150 Ω^{-1} cm^2 mol^{-1}. EPR (CH_2Cl_2/toluene, 77 K): $g_\perp = 2.20$ $A_\perp = 98 \times 10^{-4}$ cm^{-1}. Magnetism (solid state, room temperature): μ_{RT} = 1.96 μ_B/Cu.

Proof for the Presence of CH_2Cl_2 in $[Cu(TMPA)(m\text{-}ClC_6H_4C(O)O^-](PF_6){\cdot}0.5CH_2Cl_2$ (6). Complex **6** was reduced by KCN in CD_3NO_2 in a manner similar to that described for **1**. ^1H NMR (CD_3NO_2): δ 3.80 (s, 6 H), 5.33 (s, CH_2Cl_2), 7.00−8.00 (m, 13 H), 8.52 (d, 3 H).

Synthesis of $[Cu(Me_2im)_3(m\text{-}ClC_6H_4C(O)OO^-)](PF_6)$ (2). A solution of $[Cu(Me_2im)_3](PF_6)$ (**7**) (0.35 g, 0.71 mmol) in CH_2Cl_2 was oxygenated by bubbling with O_2 for 10 min at −90 °C, to form a brown solution of $[Cu_2(Me_2im)_6(O_2)]^{2+}$ (**8**). Excess O_2 was removed from the brown solution by repeated vacuum/Ar applications, and *m*-chloroperoxybenzoic acid (0.13 g, 0.75 mmol) was added as a solid to the solution at −90 °C. An immediate color change to deep green occurred, and the green solution was stirred for 4 h at −90 °C. Slow addition of diethyl ether (200 mL) to the green solution at −90 °C generated a green precipitate, which was washed with Et_2O (2 × 30 mL) and dried under vacuum. This was recrystallized at −90 °C with CH_2Cl_2/Et_2O (1:4 v/v) giving the product (0.32 g, 68%) that was stable as solid at room temperature. Anal. Calcd for $C_{22}H_{28}ClCuF_6N_6O_3P$: C, 39.52; H, 4.20; N, 12.57. Found: C, 39.36; H, 4.26; N, 12.37. IR (Nujol, cm^{-1}): 1745 (m, C=O), 845 (vs, PF_6^-). UV−vis [CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 409 (sh, 290), 670 (130). Molar conductivity: Λ_M = 145 Ω^{-1} cm^2 mol^{-1}. EPR (CH_2Cl_2/toluene, 77 K): $g_\perp = 2.04$, $g_\parallel = 2.26$, $A_\parallel = 180 \times 10^{-4}$ cm^{-1}. Magnetism (solid state, room temperature): μ_{RT} = 1.80 μ_B/Cu

Reaction of $[Cu(Me_2im)_3(m\text{-}ClC_6H_4C(O)OO^-)](PF_6)$ (2) with PPh_3. A solution of $[Cu(Me_2im)_3(m\text{-}ClC_6H_4C(O)OO^-](PF_6)$ (**2**) (0.10

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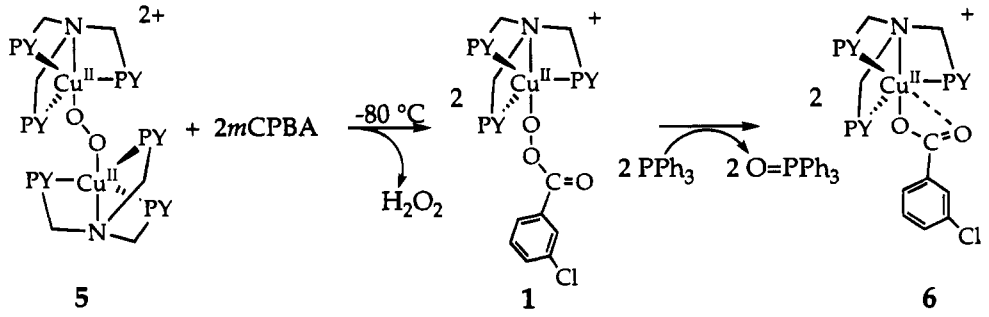
Scheme 3



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g, 0.15 mmol) was prepared in 15 mL of CH_2Cl_2 at −80 °C, and PPh_3 (0.08 g, 0.31 mmol) was added to the green solution. This solution was stirred at −80 °C for 2 h, and a slow color change to blue was observed. The blue solution was warmed to room temperature, and Et_2O (50 mL) was added to yield a blue precipitate. The supernatant was subjected to gas chromatographic analysis, showing a mixture of 44% O=PPh_3/56% PPh_3 (yield of O=PPh_3 = 88%)) when compared to a previously prepared 50:50 mixture of PPh_3/O=PPh_3.

Low-Temperature Solution FT-IR Spectroscopy: Characterization of [Cu(CPY2-O$^-$)(*m*-ClC$_6$H$_4$C(O)OO$^-$)] (3). The solution FT-IR spectroscopy was performed on a ReactIR 1000 Reaction Monitoring System developed by Spectra-Tech (Applied Systems, Inc., Annapolis, MD). The system is composed of two parts, the reaction bench and the data analysis system. A Fourier transform infrared spectrophotometer is integrated into the base of the reaction bench. Two KBr windows are mounted on the top of the reaction bench, through which the modulated infrared beam can pass into a specially designed internal reflectance element comprising a ZnSe crystal. When a reaction mixture is in contact with the ZnSe crystal, at each point of reflection an evanescent wave penetrates approximately one-half wavelength into the liquid media. The overall internal reflections through the ZnSe crystal define the path length. The ZnSe crystal is mounted on a steel disk that fits into the bottom of the reaction vessel.

The reaction vessel contains two parts. The bottom part consists of a double-jacketed hollow glass cylinder with optically polished extended surfaces on top and bottom to permit easy sealing. This part can be mounted on the ZnSe crystal and fastened with metal clips on a specially designed metal base. The top part is a double-jacketed hollow glass piece with extended optically polished surface on one end that can sit on the other part and secured with a metal clamp. The top part is equipped with five necks: a central neck (No. 11 Ace thread) for inserting a glass stirring shaft, two necks with No. 7 Ace thread for inserting a glass cooling coil, and two 14/20 female joints for air-sensitive manipulations. The stirring shaft is driven by a T-Line stirring motor. The solution inside the reaction vessel is cooled to a desired temperature by circulating cold methanol through the glass coil from a Neslab ULT95DD Endocal circulating bath.

The data analysis system was a Compaq 386/e computer directly interfaced with the reaction bench. Special software was supplied by Spectra-Tech which could assist in data acquisition from the bench with further data analysis. The computer was connected to a Hewlett-Packard ColorPro plotter.

In a typical experiment, CH_2Cl_2 (~60 mL) was added to the reaction vessel under Ar and was cooled to −75 °C by turning on the circulating bath. Two precautionary measures observed at this point were (1) the solvent should always be stirred and (2) a flow of Ar should be maintained around and below the reaction vessel to keep out moist air. Failure to take the second measure led to fogging on the ZnSe crystal, resulting in hindrance of the reflected beam for detection. Once the solvent was cooled, a spectrum was acquired and stored as background. The solvent was slowly warmed to room temperature by shutting off the circulating unit (usually requiring 2−3 h). The reaction vessel was charged with [Cu(CPY2-O$^-$)(Cl)]·2H_2O (**9**) (0.80 g, 1.80 mmol) and cooled to −75 °C, and a spectrum of the resulting brown solution was obtained. Under a flow of Ar, *m*-chloroperoxybenzoic acid was added to the reaction vessel, and a fast color change to dark green was observed. An IR spectrum of the green solution was acquired at this stage, and the solution was warmed to the room temperature to decompose the product. At room temperature, a brownish-green solution developed that was again cooled to −75 °C, and a spectrum was recorded.

Synthesis of the Carboxylato Complex [Cu(CPY2-O$^-$)(*m*-ClC$_6$H$_4$C(O)O$^-$)] (10). A solution of [Cu(CPY2-O$^-$)(Cl)]·2H_2O (**9**) (0.25 g, 0.54 mmol) was prepared in 30 mL of CH_2Cl_2 under Ar and was cooled to −80 °C. To the resulting brown solution was added *m*-chloroperoxybenzoic acid (0.10 g, 0.58 mmol) as a solid, and the color of the solution slowly changed to deep green over a period of *ca.* 30 min. Triphenylphosphine (0.29 g, 1.10 mmol) was added to the green solution at −80 °C, and after ~15 min of stirring, the color of the solution slowly changed to brownish-green. Addition of diethyl ether (200 mL) and recrystallization from CH_2Cl_2/Et_2O (1:3, v/v) yielded a brownish-green microcrystalline product (0.24 g, 80%). The Et_2O supernatant was analyzed by gas chromatography, revealing a 55:45 PPh_3:O=PPh_3 mixture (90% conversion). Anal. Calcd for $C_{28}H_{26}ClCuN_3O_3$: C, 60.98; H, 4.72; N, 7.60. Found: C, 60.72; H, 4.87; N, 7.05. IR (Nujol, cm^{-1}): 1578 (s, C=O$_{asym}$), 1605 (s, C=C). UV−vis [CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 249 (16 000), 286 (sh, 8200), 446 (840), 651 (125). Molar conductivity: Λ_M = 36 Ω^{-1} cm^2 mol^{-1}. EPR (CH_2Cl_2/toluene, 77 K): $g_\perp$ = 2.04, $g_\parallel$ = 2.27, $A_\parallel$ = 165 × 10^{-4} cm^{-1}. Magnetism (solid state, room temperature): μ_{RT} = 1.78 μ_B/Cu

Results and Discussion

[Cu(TMPA)(*m*-ClC$_6$H$_4$C(O)OO$^-$)]$^+$ (1). Oxygenation of [Cu^I(TMPA)(RCN)]$^+$ (**4**) at low temperature generates a purple {Cu_2−O_2} species [{Cu^{II}(TMPA)}$_2$(O_2^{2-})]$^{2+}$ (**5**) that has a *trans*-μ-1,2-peroxo bridging ligand between two monocopper(II) units.[31] The peroxo group in **5** is nucleophilic in nature and reacts readily with acids to give H_2O_2.[35] When a solution of [{Cu^{II}(TMPA)}$_2$(O_2^{2-})]$^{2+}$ (**5**) in CH_2Cl_2 at −80 °C is reacted with *m*-chloroperoxybenzoic acid, an immediate color change to blue is observed. Precipitation with diethyl ether gave a blue solid formulated as [Cu(TMPA)(*m*-ClC$_6$H$_4$C(O)OO$^-$)]$^+$ (**1**) (Scheme 3); hydrogen peroxide is generated through this acid−base reaction, and this was detected qualitatively (Experimental Section).

Compound **1** is stable at room temperature as a solid for *ca.* 2 weeks and, in solution, only at temperatures <−60 °C. The formulation of **1** as a mononuclear acylperoxo−Cu(II) complex is based on various lines of evidence. The infrared (mull) spectrum of **1** exhibits a typical carbonyl stretching frequency at 1740 cm^{-1}, suggesting that the C=O group on the *m*-CPBA ligand does not bind to the copper ion and that the perbenzoato group binds as a unidentate oxygen donor ligand. This carbonyl stretching frequency is comparable to that of free *m*-CPBA (1735 cm^{-1}). Compound **1** possesses a room-temperature magnetic moment μ_{RT} = 2.00 μ_B/Cu, consistent with an uncoupled and mononuclear paramagnetic d^9 system, and solution conductivity measurements show it to be a 1:1 electrolyte (Experimental Section).

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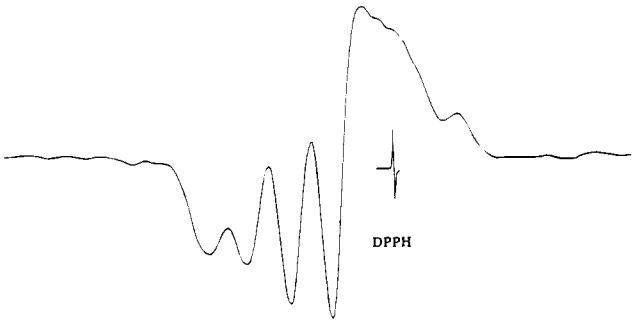

Figure 1. EPR spectrum of [Cu(TMPA)(*m*-$ClC_6H_4C(O)OO^-$)]$^+$ (**1**) at 77 K in CH_2Cl_2/toluene.

The UV−vis spectrum of [Cu(TMPA)(*m*-$ClC_6H_4C(O)OO^-$)]$^+$ (**1**) gives a low-energy band at 870 nm (ϵ 280 M^{-1} cm^{-1}) with a high-energy shoulder at 690 nm (ϵ, 160 M^{-1} cm^{-1}). The presence of a low-energy d−d band with a high-energy shoulder is typical of trigonal-bipyramidal Cu(II) complexes; tetragonally coordinated species exhibit a reversed appearance of band maximum and shoulder.[34,36−39] The UV−vis data are comparable to those of a crystallographically characterized mononuclear complex [Cu(TMPA)(Cl)]$^+$ (962 nm (ϵ 210), 632 sh nm (ϵ 88)), which has a nearly perfect trigonal-bipyramidal geometry.[34,36] Complex **1** also exhibits a stronger absorption at 332 nm (ϵ 950 M^{-1} cm^{-1}) that is tentatively assigned to a *m*-$ClC_6H_4C(O)OO^-$ → Cu(II) charge transfer transition. The frozen solution electron paramagnetic resonance (EPR) spectrum of **1** (Figure 1) is also typical of trigonal-bipyramidal Cu(II) complexes, having a "reverse axial" appearance with $g_\perp > g_\parallel \sim 2.0$ and $|A_\parallel| = 60-100 \times 10^{-4}$ cm^{-1}.[34,36,40−43] The $g_\perp$ (2.16) and $A_\perp$ (85×10^{-4} cm^{-1}) values are comparable to those of other [Cu^{II}(TMPA)(D)]$^{n+}$ (D = anionic or neutral donor; n = 1, 2).[34,36,44] The lack of well-defined hyperfine splitting in the parallel region of the spectrum prevents accurate determination of $g_\parallel$ and $A_\parallel$.

Complex **1** reacts with PPh_3 at −80 °C in CH_2Cl_2 to quantitatively yield O=PPh_3 and a mononuclear carboxylato complex [Cu(TMPA)(*m*-$ClC_6H_4C(O)O^-$)]$^+$ (**6**) (Scheme 3). The isolated blue complex **6** does not have the 1740 cm^{-1} peak in its IR spectrum, but rather a new peak is seen at 1620 cm^{-1}. This band is attributable to the carbonyl group on the benzoato ligand that is uncoordinated or weakly interacting with the Cu(II) ion. The high $\nu_{C=O}$ value for **6** suggests that the carboxylate group is not binding symmetrically as a bidentate ligand. For a symmetrically bound benzoato group, such as in [Cu(HB(3,5-*i*$Pr_2pz)_3$)(*m*-$ClC_6H_4C(O)OO^-$)] described by Kitajima *et al.*, the $\nu_{C=O}$ stretch occurs at ~1515 cm^{-1}.[29] The EPR spectrum of **6** also shows a reversed axial appearance (see Experimental Section) like that of **1**, suggesting a trigonal-bipyramidal geometry for the Cu(II) ion. The oxidation of PPh_3 by **1** may involve either a metal complex based reaction or an initial dissociation of the −OOR group (upon warming?) followed by a direct attack on the substrate. Further detailed mechanistic studies have not been carried out.

[Cu(Me$_2$im)$_3$(*m*-$ClC_6H_4C(O)OO^-$)]$^+$ (2). The second mononuclear acylperoxo complex synthesized in this series is derived from the {Cu_2O_2} species [Cu_2(Me$_2$im)$_6$(O_2)]$^{2+}$ (**8**), formed by low-temperature oxygenation of {Cu^I((Me$_2$im)$_3$]$^+$ (**7**).[32] Complex **8** also possesses a peroxo group which is nucleophilic in behavior;[32] thus reaction with *m*-CPBA was expected to proceed in a manner similar to that described for [{Cu(TMPA)}$_2$(O_2)]$^{2+}$ (**5**). When a brown solution of [Cu_2(Me$_2$im)$_6$(O_2)]$^{2+}$ (**8**) in CH_2Cl_2 at −90 °C is treated with *m*-chloroperoxybenzoic acid, an immediate color change to dark green occurs. The isolated green compound [Cu(Me$_2$im)$_3$(*m*-$ClC_6H_4C(O)OO^-$)]$^+$ (**2**) displays a carbonyl stretching frequency in the infrared region at 1745 cm^{-1}, suggesting that the C=O group does not interact with the copper ion (Scheme 4).

The mononuclear nature of [Cu(Me$_2$im)$_3$(*m*-$ClC_6H_4C(O)OO^-$)]$^+$ (**2**) is evidenced by its room-temperature magnetic moment (Experimental Section), solution conductivity (1:1 electrolyte), and a normal (i.e., tetragonal) EPR spectrum, similar to that of the mononuclear complex [Cu(Me$_2$im)$_4$]$^{2+}$ with $g_\perp$ = 2.04, $g_\parallel$ = 2.26, and $A_\parallel = 180 \times 10^{-4}$ cm^{-1}.[45] Complex **2** is stable at room temperature as a solid and reacts with PPh_3 at −90 °C in *ca.* 2 h to quantitatively yield O=PPh_3 and a blue Cu(II) product. We were unable to identify or purify the latter, probably due to complications and multiple equilibria involving the unidenate imidazole ligands.

[Cu^{II}(CPY2-O^-)(*m*-$ClC_6H_4C(O)OO^-$)] (3). The third mononuclear acylperoxo−Cu(II) complex is generated from the tetradentate phenol-derived ligand CPY2-O^-.[33,46] When a brown solution of [Cu(CPY2-O^-)(Cl)]·2H_2O (**9**) is reacted with *m*-CPBA at −75 °C, an immediate color change to dark green is observed. All attempts to isolate the green species failed due to its extreme thermal sensitivity. The reaction was therefore monitored by low-temperature solution FT-IR spectroscopy (Experimental Section), and the results are displayed in Figures 2 and 3. When ~1 equiv of *m*-CPBA is added to a −75 °C CH_2Cl_2 solution of **9**, the color change to dark green is accompnied by the development of a pronounced new IR absorption band at ~1750 cm^{-1}. This peak is ascribed to the carbonyl C=O stretch for a Cu(II)-coordinated peroxybenzoato anion in [Cu^{II}(CPY2-O^-)(*m*-$ClC_6H_4C(O)OO^-$)] (**3**) (Scheme 5). When this solution is warmed to the room temperature, it becomes brown, and recooling to −75 °C results in the formation of spectrum 2, Figure 3, showing the disappearance of the peak at 1750 cm^{-1}, while a new absorption appears at ~1565 cm^{-1}. This latter band is assigned to an unsymmetrically bound RCO_2^- carboxylato group in the product [Cu(CPY2-O^-)(*m*-$ClC_6H_4C(O)O^-$)] (**10**).[29] These results suggest that a metastable acylperoxo species **3** is observed at low temperature, but this thermally decomposes to give the carboxylato complex [Cu(CPY2-O^-)(*m*-$ClC_6H_4C(O)O^-$)] (**10**).

The compound [Cu(CPY2-O^-)(*m*-$ClC_6H_4C(O)O^-$)] (**10**) was also independently synthesized. When [Cu(CPY2-O^-)(*m*-$ClC_6H_4C(O)OO^-$)] (**3**) is generated at −80 °C as described above and PPh_3 is added, the color of the solution changes to greenish-brown in *ca.* 15 min at this temperature. A small aliquot of the solution can be used to show (GC analysis) that O=PPh_3 is formed quantitatively. Thus, in the absence of

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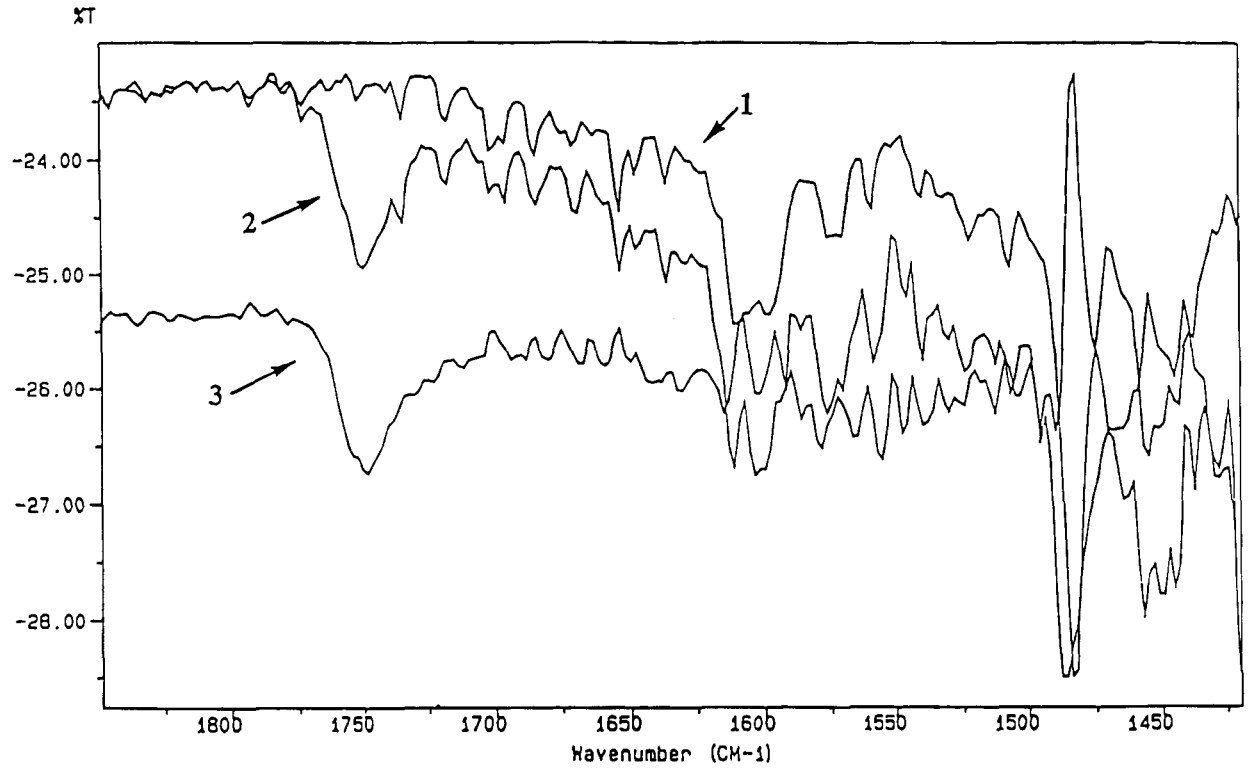
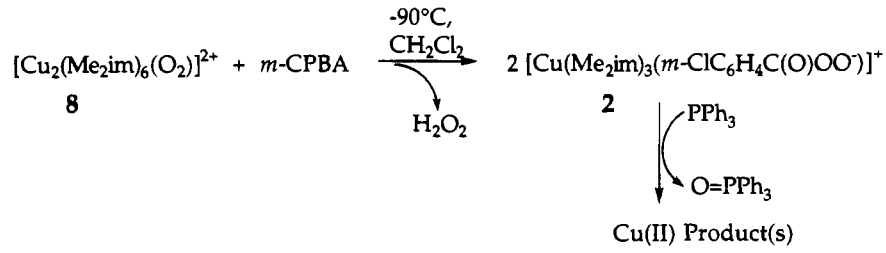
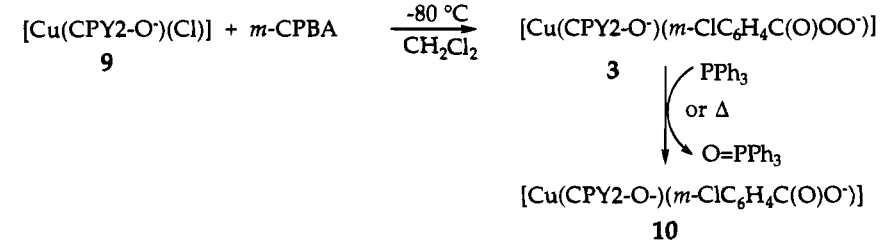


Figure 2. Low-temperature (−75 °C) solution FT-IR spectra of [Cu(CPY2-O$^-$)(Cl)]·2H$_2$O (**9**) (spectrum 1) and [Cu(CPY2-O$^-$)(*m*-ClC$_6$H$_4$C(O)OO$^-$)] (**3**) (spectrum 2) and the difference of spectra 1 and 2 (spectrum 3) in CH$_2$Cl$_2$ (CH$_2$Cl$_2$ as the background). Note the appearance of a peak at 1748 cm^{-1} for **3**.

Scheme 4



Scheme 5



further mechanistic work, it appears that direct reaction of **3** and PPh$_3$ substrate occurs. A greenish-brown complex can be isolated from the mixture (Experimental Section), and this netural complex has analytical and spectroscopic (i.e., EPR, magnetic moment) properties conforming to the mononuclear formulation [Cu(CPY2-O$^-$)(*m*-ClC$_6$H$_4$C(O)O$^-$)] (**10**).

The vis spectrum of [Cu(CPY2-O$^-$)(*m*-ClC$_6$H$_4$C(O)O$^-$)] (**10**) isolated in this manner {λ (ϵ, M^{-1} cm^{-1}): 446 (840), 650 (125) nm)} is similar to that observed for the decomposition product described in the low-temperature solution FT-IR spectroscopic experiment {vis spectrum, λ (ϵ, M^{-1} cm^{-1}): 440 (800), 645 (140) nm). The mull IR spectrum of isolated complex **10** exhibits a band at 1578 cm^{-1} assigned to a carboxylate group weakly coordinating to Cu(II). The peak position is ~10 cm^{-1} higher than that seen from the solution IR spectrum; this can probably be ascribed to different conditions of measurement, including temperature (room vs −75 °C) and medium (mull vs solution).

Summary/Conclusions

The acylperoxo–Cu(II) species [Cu(TMPA)(*m*-ClC$_6$H$_4$C(O)OO$^-$)]$^+$ (**1**) and [Cu(Me$_2$im)$_3$(*m*-ClC$_6$H$_4$C(O)OO$^-$)]$^+$ (**2**) described here seem to have enhanced reactivity toward substrate (PPh$_3$), compared to their peroxo–dicopper(II) dinuclear counterparts [{Cu(TMPA)}$_2$(O$_2$)]$^{2+}$ (**5**) and [Cu$_2$(Me$_2$im)$_6$(O$_2$)]$^{2+}$ (**8**). Both **5** and **8** do not transfer an oxygen atom to PPh$_3$; rather, Cu(I)–phosphine adducts are formed while dioxygen is liberated.[32,35] The enhanced reactivity exhibited by these LCu^{II}–OOC(O)R complexes is in accord with that observed for other transition-metal peroxide species, where the

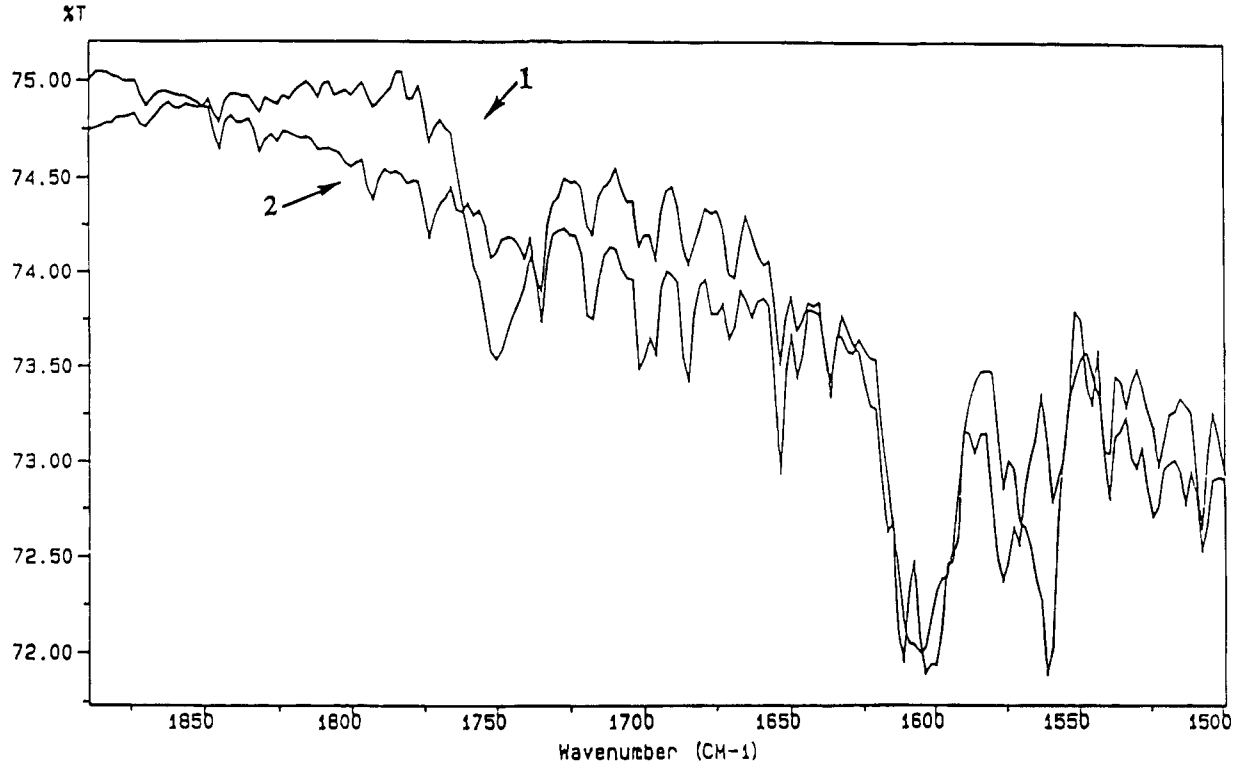


Figure 3. Low-temperature (−75 °C) solution FT-IR spectra of [Cu(CPY2-O$^-$)(*m*-ClC$_6$H$_4$C(O)OO$^-$)] (**3**) (spectrum 1) and its decomposition product [Cu(CPY2-O$^-$)(*m*-ClC$_6$H$_4$C(O)O$^-$)] (**10**) (spectrum 2) in CH_2Cl_2 (CH_2Cl_2 as the background). Note the disappearance of the 1748 cm^{-1} peak and the appearance of a new peak at 1565 cm^{-1} for **10**.

oxidation of substrates is enhanced by the presence of electrophiles, e.g. H^+ or $RC(O)^+$.[47-51] We have described a similar situation occurring for the dicopper(II)−OOR′ (R′ = H−, RC(O)−) complexes $[Cu_2(XYL\text{-}O^-)(OOR')]^{2+}$ mentioned previously (see Introduction).[26] The electrophilic activation of (porphyrin)M−O_2 complexes (possible models for cytochrome P-450) has been described, where heterolytic and/or homolytic cleavage of the O−O bond leads to reactive metal−oxo oxidizing agents.[52-55] In the present case, however, further mechanistic work is required to deduce the mechanism for PPh_3 oxidation involved. A future direction in this research lies in testing the reactivity of these species with other substrates, e.g. olefins, amines and hydrocarbons. The compound [Cu(CPY2-O$^-$)(*m*-ClC$_6$H$_4$C(O)OO$^-$)] (**3**) would seem to be the best bet for such studies since it is the most unstable (i.e., reactive), on the basis of its reaction with PPh_3, which is faster than that observed for **1** or **2**, and it even appears to proceed at low-temperature.

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