Independent Synthesis and Structural Characterization of a Mononuclear Copper−Hydroxide Complex Previously Assigned as a Copper−Superoxide Species

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Introduction

Mononuclear 1:1 $Cu-O_2$ adducts are key postulated intermediates in numerous important biological and catalytic processes, such as reversible dioxgyen binding by copper complexes and dioxygen activation by synthetic compounds and metalloproteins.[1] As a result, the elucidation of the nature of such adducts has been a central objective in bioinorganic chemistry research, with specific recent emphasis on identifying them through kinetics investigations[2] and on using ligand design principles to enable their isolation and structural characterization.[3,4] Only two X-ray crystal structures of 1:1 $Cu-O_2$ complexes have been reported, $Tp^{tBu,iPr}Cu(O_2)$ [$Tp^{tBu,iPr}$ = tris-(3-*tert*-butyl-5-isopropylpyrazolyl)hydroborate], in which η^2 "side-on" coordination of the superoxide was identified and spectroscopically verified,[3] and $[Cu(tppa)(O_2)]ClO_4$ (tppa = tris-[(6-(pivaloylamido)-2-pyridyl)methyl]amine), which was represented as having a η^1 "end-on" superoxide stabilized by hydrogen-bonding interactions with the surrounding pivaloylamide ligand substituents (Figure 1).[4] Reexamination of the published X-ray data for the latter complex suggested that the data were incorrectly interpreted and that, instead, it is a monocopper hydroxide complex. In support of this hypothesis, we have independently synthesized and structurally characterized the compound, which itself is a unique example of a $Cu^{II}-OH$ species stabilized by intramolecular hydrogen-bonding interactions of relevance to metalloprotein active-site chemistry.

Experimental Section

The general procedures used for solvent purification and synthetic manipulations were as previously described.[5]

Safety Note. *Caution*! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great care.

Tris[(6-(pivaloylamido)-2-pyridyl)methyl]amine (tppa). This ligand was prepared according to a published method,[6] but with the following modifications and/or important unreported details. 2-(Pivalolylamido)-6-methylpyridine was prepared as described. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.02 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H) 2.42 (s, 3H), 1.29 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 177.1, 156.6, 150.9, 138.7, 119.1, 110.8, 39.8, 27.5, 23.9 ppm. GC-MS: M^+, *m/z* 192. Bromination on a 7.0 g (0.036 mol) scale with NBS also proceeded similarly to the published method (3.22 g of NBS, 50 mg of AIBN, 200 mL of CCl_4; irradiated with a projector lamp for 24 h) to yield 2-(pivalolylamido)-6-(bromomethyl)pyridine, which was isolated after chromatography (20% EtOAc/hexanes, 230−400 mesh silica gel, R_f = 0.50; impurities have R_f = 0.35 and 0.83) as an orange oil (1.3 g, 13%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.17 (d, J = 8.0 Hz, 1H), 8.01 (br, 1H), 7.68 (t, J = 8.0 Hz, 1H), 7.13 (d, J = 8.0 Hz, 1H), 4.42 (s, 2H), 1.32 (s, 9H) ppm. GC-MS: M^+, *m/z* 270. Treatment of this oil with potassium phthalimide yielded 2-(pivaloylamido)-6-(phthalimidomethyl)pyridine as reported, which on a 1.65 g (0.0048 mol) scale was refluxed with hydrazine hydrate (240 μL, 0.0063 mol) in EtOH (25 mL) for 3 h. The solution was then cooled to ambient temperature, and its volume was reduced by half in vacuo. To this solution were added H_2O (20 mL) and 6 M HCl until the solution had a pH of 1. Subsequent heating to ∼80 °C for 2 h led to the appearance of a white precipitate (phenylhydrazide). After cooling of the reaction mixture to room temperature, the solution was filtered and the filtrate treated with aqueous NaOH until the solution had a pH of >11. Extraction with $CHCl_3$ (3 × 50 mL), drying of the combined $CHCl_3$ fractions with Na_2SO_4, and removal of the solvent under reduced pressure yielded 2-(pivaloylamido)-6-(aminomethyl)pyridine as a yellow solid (0.709 g, 70%; lit. yield 74%).[6] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.06 (d, J = 8.0 Hz, 1H), 7.96 (br, 1H), 7.61 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 8Hz, 1H), 3.86 (br, 2H), 2.09 (br), 1.29 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 177.2, 159.9, 151.2, 138.9, 116.9, 111.9, 47.2, 39.8, 27.5. GC-MS: M^+, *m/z* 207. This compound (0.123 g, 5.94×10^{-4} mol) was then treated with 2-(pivaloylamido)-6-(bromomethyl)-pyridine (0.326 g, 1.20×10^{-3}) in CH_3CN (20 mL). Following addition of Na_2CO_3 (0.245 g, 2.31×10^{-3} mol) and NBu_4Br (5 mg), the solution was heated at reflux overnight. The reaction mixture was cooled to room temperature and filtered, remaining solid was washed with CH_2Cl_2, and the combined organic filtrates were dried (Na_2SO_4) and brought to dryness under reduced pressure to yield tppa (0.270 g, 79%; lit. yield 30%)[6] with NMR spectroscopic properties identical to those reported.

[(tppa)Cu(OH)]ClO_4. To a CH_3CN (3 mL) solution of tppa (42.3 mg, 7.21×10^{-2} mmol) was added a CH_3CN (3 mL) solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (26.5 mg, 7.15×10^{-2} mmol), resulting in the formation of a deep green solution upon stirring for 5 min at room temperature. To this solution was added an equal volume of 1 N NaOH. The resulting mixture was stirred vigorously for 5 min. The solution was then allowed to settle, and the aqueous phase was removed by pipet. To the remaining bright green organic phase was added an equal volume of water, plus acetone (2 mL) and excess (∼0.5 g) $NaClO_4$. Allowing the resulting mixture to evaporate slowly over the course of several days led to the deposition of a blue-green precipitate floating in the remaining water. X-ray-quality crystals were obtained by redissolving

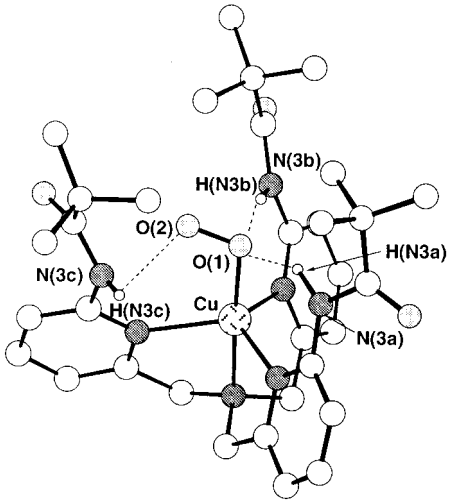

Figure 1. Chem3D representation of the reported X-ray crystal structure of $[(tppa)Cu(O_2)]ClO_4$, drawn from the published coordinates.[4]

(1) Recent reviews: (a) Kitajima, N.; Moro-oka, Y. *Chem. Rev.* **1994**, *94*, 737−757. (b) Karlin, K. D.; Tyeklár, Z. *Adv. Inorg. Biochem.* **1994**, *9*, 123−172. (c) Fox, S.; Karlin, K. D. In *Active Oxygen in Biochemistry*; Valentine, J. S., Foote, C. S., Greenberg, A., Liebman, J. F., Eds.; Blackie Academic & Professional, Chapman & Hall: Glasgow, Scotland, 1995; pp 188−231.

(2) Karlin, K. D.; Wei, N.; Jung, B.; Kaderli, S.; Niklaus, P.; Zuberbühler, A. D. *J. Am. Chem. Soc.* **1993**, *115*, 9506−9514.

(3) Fujisawa, K.; Tanaka, M.; Moro-oka, Y.; Kitajima, N. *J. Am. Chem. Soc.* **1994**, *116*, 12079−12080.

(4) Harata, M.; Jitsukawa, K.; Masuda, H.; Einaga, H. *J. Am. Chem. Soc.* **1994**, *116*, 10817−10818.

(5) Halfen, J. A.; Mahapatra, S.; Wilkinson, E. C.; Gengenbach, A. J.; Young, V. G., Jr.; Que, L., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1996**, *118*, 763−776.

(6) Harata, M.; Jitsukawa, K.; Masuda, H.; Einaga, H. *Chem. Lett.* **1995**, 61−62.

S0020-1669(96)00340-0 CCC: $12.00

Table 1. Summary of X-ray Crystallographic Details for [(tppa)Cu(OH)]ClO_4

empirical formula	$C_{33}H_{46}ClCuN_7O_8$
fw	767.76
crystal system	orthorhombic
space group	Pccn
a (Å)	11.2979(2)
b (Å)	35.3335(6)
c (Å)	18.2702(2)
V (Å$^{3)}$	7293.4(2)
Z	8
D_c (g/cm^3)	1.398
temp (K)	173(2)
crystal size (mm)	0.50 × 0.28 × 0.17
diffractometer	Siemens SMART
radiation (λ (Å))	Mo Kα (0.710 73)
abs coeff (mm^{-1})	0.731
2θ max (deg)	49.96
no. of reflns collected	34077
no. of ind reflns	6419
no. of obs reflns	5736
no. of parameters	533
R_1[a] [$I > 2\sigma(I)$]	0.0464
wR_2[b]	0.0992
goodness-of-fit[c]	1.120
largest diff peak and hole (e Å^{-3})	0.944, −0.608

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, where $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$; $a = 0.030\ 00$, $b = 13.2659$, and $P = (F_o^2 + 2F_c^2)/3$. [c] GOF $= [\Sigma(|F_o| - |F_c|)^2/\Sigma(N_{reflns} - N_{params})]^{1/2}$.

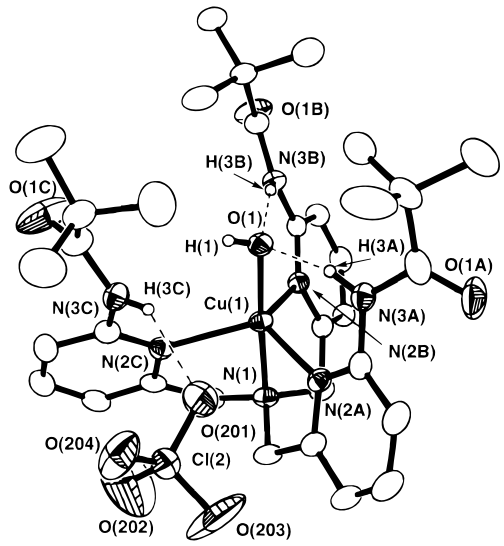

Figure 2. Representation of the X-ray crystal structure of independently prepared [(tppa)Cu(OH)]ClO_4 (50% thermal ellipsoids; all hydrogen atoms except for the hydroxide and amide hydrogens omitted for clarity). Selected bond distances (Å) and angles (deg): Cu(1)−O(1), 1.878(2); O(1)−H(1), 0.71(4); Cu(1)−N(1), 2.002(2); Cu(1)−N(2A), 2.114(2); Cu(1)−N(2B), 2.152(2); Cu(1)−N(2C), 2.182(2); Cu(1)−O(1)−H(1), 108(3); O(1)−Cu(1)−N(1), 176.08(10); O(1)−Cu(1)−N(2A), 98.88(9); O(1)−Cu(1)−N(2B), 96.49(9); O(1)−Cu(1)−N(2C), 103.93(9); N(1)−Cu(1)−N(2A), 81.51(9); N(1)−Cu(1)−N(2B), 80.02-(9); N(1)−Cu(1)−N(2C), 79.29(9); N(2A)−Cu(1)−N(2B), 120.34(9); N(2A)−Cu(1)−N(2C), 115.83(9); N(2B)−Cu(1)−N(2C), 115.46(8).

the precipitate in acetone (2 mL) and water (6 mL), adding more $NaClO_4$, and again allowing slow evaporation at room temperature, yielding the final product as blue-green crystalline blocks (27 mg, 50%). UV−vis (MeOH) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 316 (6700), 444 (160), 650 (140), 732 (150). FTIR (KBr, cm^{-1}): 3622 (ν_{O-H}), 3332 (br, ν_{N-H}), 3072, 2973, 2873, 1694 ($\nu_{C=O}$), 1608, 1585, 1537, 1471, 1447, 1410, 1369, 1310, 1283, 1229, 1159, 1098 (ν_{ClO_4}), 1029, 1005, 901, 814, 790, 656, 623 (ν_{ClO_4}), 539. ISP-MS (CH_2Cl_2), *m/z* (relative intensity): 667.3 ([M − ClO_4]$^+$, 75%), 685.3 ([M − ClO_4+H_2O]$^+$, 20%). EPR (1:1 CH_3CN−toluene, −154 °C, 9.46 GHz): $g_1 = 2.22$, $g_2 = 2.10$, $g_3 = 2.03$, $A_1^{Cu} = 145$ G (values from preliminary spectral simulation using methods previously described;[7] see Figure S1, Supporting Information). Anal Calcd for $C_{33}H_{46}N_7O_8CuCl$: C, 51.68; H, 6.05; N, 12.79. Found: C, 51.45; H, 5.92; N, 12.66.

[(tppa)Cu](ClO_4). To a solution of tppa (54.9 mg, 9.36×10^{-2} mmol) in CH_3CN (2 mL) was added [Cu(CH_3CN)$_4$]ClO_4 (29.4 mg, 8.99×10^{-2} mmol) under a N_2 atmosphere. The mixture was stirred at room temperature overnight, resulting in the formation of a yellow solution. This solution was then pumped to dryness and the remaining oil triturated with pentane to give the product as a yellow solid (45.0 mg, 67%). ^{1}H NMR (CD_3CN, 300 MHz): δ 8.17 (br, 3H), 8.05 (d, J = 8.0 Hz, 3H), 7.79 (t, J = 8.0 Hz, 3H), 7.13 (d, J = 8.0 Hz, 3H), 4.04 (s, 6H), 1.29 (s, 27H) ppm. ^{13}C{^{1}H} NMR (CD_3CN, 75 MHz): δ 176.9, 155.6, 150.6, 139.7, 119.6, 113.7, 59.7, 39.7, 23.3 ppm. ^{1}H NMR (CD_3OD, 500 MHz): 7.85 (br m, 6H), 7.16 (d, J = 8.0 Hz, 3H), 4.01 (s, 6H), 1.29 (s, 27H) ppm. FTIR (KBr, cm^{-1}): 3350 (ν_{N-H}), 2972, 2939, 2873, 1696 ($\nu_{C=O}$), 1646, 1606, 1576, 1520, 1461, 1408, 1368, 1304, 1220, 1150, 1094 (ν_{ClO_4}), 799, 626 (ν_{ClO_4}). FAB-MS (MNBA), *m/z* (relative intensity): 650.3 ([M − ClO_4]$^+$, 100%).

X-ray Structure Determination of [(tppa)Cu(OH)]ClO_4. A crystal of dimensions 0.50 × 0.28 × 0.17 mm was attached to a glass fiber and mounted on the Siemens SMART system, with the cryogenic stream set to −100(2) °C for data collection. An initial set of cell constants was calculated from 92 reflections harvested from three sets of 30 frames. Final cell constants were calculated from a set of 8192 reflections from the data collection. A hemisphere collection involving the survey of a randomly oriented region of reciprocal space to the extent of 1.3 hemispheres to a resolution of 0.84 Å was performed; three major swaths of frames were collected with 0.30° steps in ω. A semiempirical absorption correction afforded minimum and maximum transmission factors of 0.575 and 0.710, respectively. See Table 1 for additional crystal and refinement information. The space group *Pccn* was determined on the basis of systematic absences and intensity statistics. A successful direct-methods solution (performed independently of that which was published)[4] was calculated which provided most non-hydrogen atoms from the *E* map. Several full-matrix least-squares/difference Fourier cycles were performed, which located the remainder of the non-hydrogen atoms. The sample was not plagued with twinning problems. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in idealized positions and were refined as riding atoms with individual isotropic displacement parameters. The perchlorate anions were restrained to a common rigid body; 33 restraints were employed. All calculations were performed using an SGI INDY R4400-SC or a Pentium computer with the SHELXTL V5.0 program suite.[8] A drawing of the complex appears in Figure 2, and selected bond lengths and angles are listed in the caption to Figure 2. Full details of the structure determination, including tables of bond lengths and angles, atomic positional parameters, and final thermal parameters for non-hydrogen atoms, are given in the Supporting Information.

Results and Discussion

Reanalysis of the published X-ray crystallographic data for the proposed superoxo complex was prompted by the large temperature factors reported for O(2) (the uncoordinated oxygen atom), the lack of supporting vibrational spectroscopic data (no ν_{O-O}), and the report that the structural characterization was carried out at room temperature, implying surprising stability for a usually quite reactive [Cu(O_2)]$^+$ moiety.[1,2] We performed a successful direct-methods solution of the structure independently of the reported atomic positions that revealed all non-hydrogen atoms except for O(2); after several cycles of refinement, no difference Fourier peak of sufficient height at the proper distance [∼1.23 Å from O(1)] to be construed as the missing O atom was found.[9] Instead, a peak corresponding to an H atom of a hydroxide ligand was located and refined

(7) Ruggiero, C. E.; Carrier, S. M.; Antholine, W. E.; Whittaker, J. W.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **1993**, *115*, 11285−11298.
(8) SHELXTL V5.0, Siemens Energy & Automation, Inc., Madison, WI 53719-1173.

isotropically. In addition, a rotational twin that went unnoticed by the original authors was accounted for in the final refinement and an improved model for the ClO_4^- anion was applied. The final refined model had a significantly lower *R* index than the published structure (5.48% vs 6.81%). Moreover, in a final check of the correctness of our model, the hydroxide H atom [H(1)] was refined as an O atom, but six cycles of least-squares refinement yielded an unrealistic O(1)−O(2) distance of 0.604 Å and $U_{iso} = 0.79$ Å^2 for O(2), a value significantly greater than those of all other non-hydrogen atoms.

Corroboration of our assessment of the published X-ray data was obtained through the independent synthesis and characterization of [(tppa)Cu(OH)]ClO_4. Treatment of an equimolar mixture of tppa and $Cu(ClO_4)_2 \cdot 6H_2O$ (0.07 mmol) with 1 M NaOH yielded a deep green solution. Addition of H_2O, acetone, and excess $NaClO_4$, followed by slow evaporation, yielded blue-green blocklike crystals of the complex (27 mg, 50% yield), the formulation of which was confirmed by CHN analysis, electrospray MS, EPR and IR spectroscopy, and X-ray crystallography (Figure 2). The X-ray structure of this independently prepared material was found to be essentially identical (albeit of higher quality) to that which we had calculated using the previously published data. The short Cu−O(1) separation of 1.878(2) Å is identical to that found in [Cu(Me$_6$tren)(OH)]-$ClO_4 \cdot H_2O$ [1.875(2) Å].[10] As in many Cu(II) complexes of tripodal tetradentate ligands akin to tppa,[11] the copper coordination geometry is approximately trigonal bipyramidal. An approximately tetrahedral geometry about O(1) is completed by the hydroxide hydrogen [located and refined isotropically, O(1)−H(1) = 0.71(4) Å] and two O···H−N bonding interactions with pivaloylamide groups characterized by the distances O(1)···N(3A) = 2.828(3) Å and O(1)···N(3B) = 2.809(3) Å. The third pivaloylamide [N(3C)] forms a hydrogen bond with a perchlorate counterion [O(201)···N(3C) = 3.029(3) Å], an arrangement that contrasts with the previously proposed interaction of this amide group with the putative O(2) of the coordinated superoxide (Figure 1). We note in passing that the array of hydrogen bonds involving the pivaloylamides and the copper hydroxide may be viewed as a model for how secondary interactions may stabilize and/or modulate the reactivity of a metal−hydroxide moiety within a metalloprotein active site.[12]

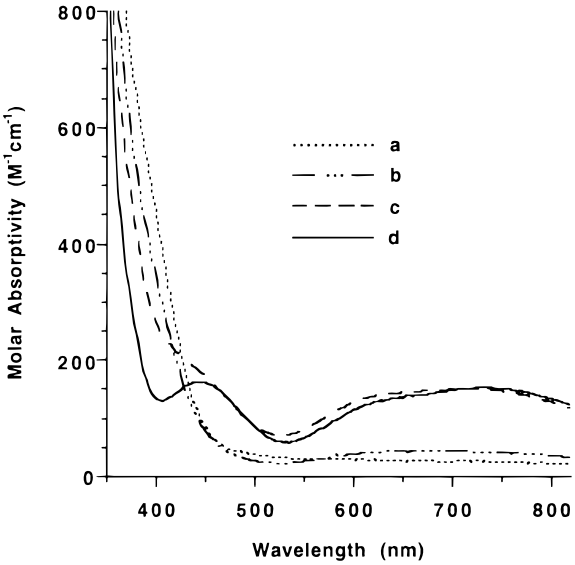

Figure 3. UV−vis spectra obtained upon treatment of equimolar amounts of tppa and $[Cu(CH_3CN)_4]ClO_4$ in MeOH at −80 °C (curve a), following oxygenation of the methanol solution at −80 °C for 30 min (curve b), after warming the oxygenated solution to ambient temperature (curve c), and upon dissolution of [(tppa)Cu(OH)]ClO_4 in MeOH at ambient temperature (curve d).

Our reassignment of the solid state structure of the supposed copper−superoxide complex raises the question of whether this species actually forms in solution as claimed on the basis of spectroscopic measurements [UV−vis λ_{max} (ϵ) = 315 (sh, ∼4000), 657 (100), 803 nm (120); EPR silent at −80 °C] and apparent reversiblity of O_2 binding.[4] In our hands, repeated attempts to oxygenate a MeOH solution of a 1:1 ratio of tppa and $[Cu(CH_3CN)_4]ClO_4$ by following the published procedure or by bubbling O_2 through a MeOH solution of the isolated complex [(tppa)Cu]ClO_4 at −80 °C did not result in reproduction of the reported spectroscopic data (Figure 3, spectra a and b). Only upon warming of the sample under O_2 did UV−vis features develop (spectrum c) which were similar to those reported, but both our and the published spectra lack the intense feature at ∼400 nm noted by Karlin for superoxo species with related ligands such as $[(TMPA)Cu(O_2)]^+$ [λ_{max} = 410 nm (ϵ ∼4000); TMPA = tris(2-pyridylmethyl)amine].[2] Moreover, the similarities between the absorption spectrum we obtained upon warming and that produced upon dissolution of pure [(tppa)-Cu(OH)]ClO_4 in MeOH (spectrum d) suggest that the Cu(II)−OH species may be a component of the oxygenated solution.[13,14] The reported lack of an EPR signal at −80 °C does not rule out this alternative explanation, since [(tppa)Cu(OH)]ClO_4 in MeOH or CH_3CN exhibits a strong rhombic EPR signal consistent with its trigonal bipyramidal structure[11,15] at −154 °C that essentially disappears upon warming to −80 °C (>90%

(9) Using the data in the Supporting Information for ref 4, the space group *Pccn* was redetermined on the basis of systematic absences and intensity statistics using SHELXTL-Plus V5.0.[8] A successful direct-methods solution was calculated which provided all non-hydrogen atoms from the *E* map with the exception of the questioned O(2). All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. The presence of a rotational twin was indicated by the number of disagreeable reflections, the most conflicting being a large number of $h = 0$, $11 \le k \le 15$ or $23 \le k \le 29$, $l = 2$, 4, 6, and 8 where $F_o \ll F_c$. Reasoning that a rotational twin about *a**:*b* [35.238-(5) Å] ≅ 2*c* [18.201(2) Å] or some other twinning operation accounted for the bad set of reflections, we omitted 10 reflections with $\Delta(F^2)$/esd quotients in the range 18.4−7.7 from the calculation (listed in Supporting Information). Finally, instead of assuming that the ClO_4^- was half-occupied and situated on a crystallographic 2-fold axis as stated in ref 4, we allowed a half-occupied generally positioned ClO_4^- to refine as a rigid group. The result was better agreement between the model and the data ($R_1 = 0.0548$ and $wR_2 = 0.1569$ for 5108 data with $I > 2\sigma(I)$, 33 restraints and 533 parameters) as well as a significant decrease in the heights of difference Fourier peaks in the vicinity of the perchlorate anion to less than 1.0 e Å^{-3}.

(10) Lee, S. C.; Holm, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 11789−11798 and ref 45 cited therein.

(11) For example, see: (a) Duggan, M.; Ray, N.; Hathaway, B.; Tomlinson, G.; Brint, P.; Pelin, K. *J. Chem. Soc., Dalton Trans.* **1980**, 1342−1348. (b) Karlin, K. D.; Hayes, J. C.; Juen, S.; Hutchinson, J. P.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 4106−4108. (c) Chuang, C.; Lim, K.; Chen, Q.; Zubieta, J.; Canary, J. W. *Inorg. Chem.* **1995**, *34*, 2562−2568.

(12) Bertini, I.; Luchinat, C. In *Bioinorganic Chemistry*; Bertini, I., Gray, H. B., Lippard, S. J., Valentine, J. S., Eds.; University Science Books: Mill Valley, CA, 1994.

(13) Additional species that may be present include a Cu(II)−OMe complex or [(tppa)Cu]$(ClO_4)_2$, the X-ray crystal structure of which reveals binding of one pivaloylamide carbonyl to the fifth available Cu(II) coordination position (see Supporting Information).

(14) The generation of copper−hydroxide complexes (typically dinuclear) upon decomposition of copper−dioxygen adducts is well-known. For example, see: (a) Mahapatra, S.; Halfen, J. A.; Wilkinson, E. C.; Que, L., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1994**, *116*, 9785−9786. (b) Mahapatra, S.; Halfen, J. A.; Wilkinson, E. C.; Pan, G.; Cramer, C. J.; Que, L., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1995**, *117*, 8865−8866.

(15) (a) Takahashi, K.; Ogawa, E.; Oishi, N.; Nishida, Y.; Kida, S. *Inorg. Chim. Acta* **1982**, *66*, 97−103. (b) Addison, A. W.; Hendriks, H. M. J.; Reedijk, J.; Thompson, L. K. *Inorg. Chem.* **1981**, *20*, 103−110.

loss in intensity). Finally, the reported observation of reversible color changes upon cycling with O_2 and CO in a MeOH-containing solution can be explained by invoking the operation of reversible redox reactions involving the solvent, a known phenomenon in copper chemistry.[16] Thus, while we cannot prove that the superoxo complex is not formed under some (as yet undefined) conditions, the lack of convincing evidence such as that which would be provided by a correct X-ray crystal structure, manometric O_2 uptake measurements, and/or vibrational spectroscopy on $^{18}O/^{16}O$-labeled isotopomers leads us to conclude that [(tppa)Cu(O_2)]ClO_4 has yet to be prepared.

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Supporting Information Available: Text giving the experimental procedure and characterization data for [(tppa)Cu]$(ClO_4)_2$, the EPR spectrum of [(tppa)Cu(OH)]ClO_4 (Figure S1), an ORTEP diagram of the cationic portion of [(tppa)Cu]$(ClO_4)_2$ (Figure S2), and full details of the X-ray crystal structure reanalysis of the published data plus the independent determinations of [(tppa)Cu(OH)]ClO_4 and [(tppa)Cu]-$(ClO_4)_2$, including tables of crystallographic experimental details, atomic coordinates, thermal parameters, bond distances, bond angles, and torsion angles (60 pages). Ordering information is given on any current masthead page.

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(16) For example, see: (a) Mahapatra, S.; Halfen, J. A.; Tolman, W. B. *J. Chem. Soc., Chem. Commun.* **1994**, 1625−1626. (b) Karlin, K. D.; Gultneh, Y. *Prog. Inorg. Chem.* **1987**, *35*, 219−328 (especially pp 273−275).