Stabilization of Copper Dioxygen Compounds: Design, Synthesis, and Characterization

Heidi Börzel,[a] Peter Comba,*[a] Charis Katsichtis,[a] Wolfgang Kiefer,[b] Achim Lienke,[a] Volker Nagel,[b] and Hans Pritzkow[a]

Abstract: Oxygenation in acetonitrile of the copper(I) complex of the rigid tetradentate, substituted bispidine ligand L^1 with a diamine-bis-pyridinyl donor set (L^1 = methyl 2,4-bis(2-pyridinyl)-3,7-diazabicyclo-[3.3.1]-nonane-9-diol-1,5-dicarboxylate) produces an end-on (μ-peroxo)dicopper(II) compound that is stable in solution up to 250 K. The spectroscopic characterization of this species (UV/visible and Raman spectroscopy) and an X-ray structural analysis of the corresponding mononuclear copper(II) compound $[Cu(L^1)Cl]^+$ indicate that the deep purple oxygenation product has two distorted square pyramidal copper(II) chromophores linked by a μ-peroxo bridge. Molecular mechanics calculations were used to interpret the relative stability of the copper dioxygen product $[\{Cu(L^1)\}_2O_2]^{2+}$ and to design the dinucleating ligand L^2, based on two L^1 binding sites, linked by an ethyl bridge. The corresponding deep purple copper dioxygen product $[Cu_2(L^2)(O_2)]^{2+}$ has spectroscopic characteristics (UV/visible and Raman spectra) that are similar but not identical to those of $[\{Cu(L^1)\}_2O_2]^{2+}$; this (μ-peroxo)dicopper(II) compound is stable at ambient temperature ($t_{1/2}$(298 K) = 50 min).

Keywords: copper · dioxygen complexes · molecular modeling · oxygen activation · oxygenations

Introduction

The activation of molecular dioxygen by metal ions is of intrinsic importance in a wide range of biological[1–6] and industrial processes.[7–10] An important first step in biological systems is the oxygen transport to the sites where O_2 is used for oxidation processes. This generally involves reversible coordination of O_2 to iron- or copper-containing proteins such as hemoglobin, myoglobin, hemerythrin, and hemocyanin.[11, 12] Oxygen activation and oxidation catalysis by O_2, mediated by metal ions, involves electron transfer from the reduced metal site to the coordinated dioxygen molecule or peroxide anion that eventually leads to O–O bond scission. Relevant biological systems include tyrosinase, catecholdioxygenase, and cytochrome P450.[11–13] A number of dioxygen binding modes have been observed and/or proposed, and for copper proteins these include mono-,[14] di-,[15–17] tri-[18] and tetranuclear[19] metal sites. Hemocyanine and tyrosinase have dinuclear copper sites with a $[Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)]^{2+}$ core (side-on peroxo bridge).[20, 21] Structural and spectroscopic studies on the copper proteins have been complemented by the synthesis and characterization of spectroscopic, structural, and functional model compounds.[1–6, 20–22] From some of these studies it emerges that other dioxygen binding modes might be of importance, namely $[Cu_2(\mu\text{-}O)_2]^{2+}$ (formal copper oxidation state of +III)[6, 17] and $[Cu_2(\mu\text{-}O_2)]^{2+}$ (end-on peroxo bridge).[5, 23] End-on (μ-peroxo)dicopper(II) model compounds are intrinsically unstable and only recently has it become possible to stabilize these species by a careful choice of solvents and/or dinucleating ligands.[24, 25] We have reported a molecular mechanics based model that allows the rational design of ligand systems that are able to stabilize copper dioxygen compounds.[26] Our aim was to develop an easily available and broadly variable ligand system for stable dioxygen binding. We report here the design, synthesis, and characterization of such ligands and of their room-temperature-stable (μ-peroxo)dicopper(II) compounds.

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Results and Discussion

Structural features and ligand design: The rigid tetradentate, substituted bispidine ligand L^1 with a diamine-bis-pyridinyl donor set (L^1 = methyl 2,4-bis(2-pyridinyl)-3,7-diazabicyclo-[3.3.1]-nonane-9-diol-1,5-dicarboxylate)[27, 28] yields four-coordinate complex fragments with an open face that is accessible for the binding and activation of substrate molecules

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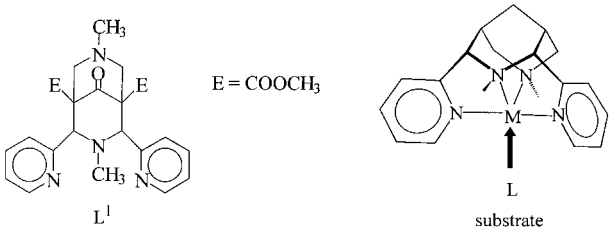

Scheme 1. Left: structure of L^1. Right: Structure of compound formed with metal.

(Scheme 1). This assumption is supported by preliminary experiments, which indicate that some of the manganese(II)[29] and some of the copper(II) compounds (vide infra)[30] are catalytically active. Stable six-coordinate $[M(L^1)X_2]^{n+}$ compounds with $M = Co^{II}$ (X_2 = bidentate ligand)[31], $M = Mn^{II}$ ($X = Cl^-$, $OSO_2CF_3^-$)[29, 30] and $M = Fe^{II}$ ($X = NCS^-$, OAc^-, pivelate + $OSO_2CF_3^-$) [32] have been isolated and analyzed by X-ray crystallography. An interesting feature is that, in general, the observed bond distances from the metal center to the two tertiary amine donors are quite different, with the bond to the amine of the pyridine-substituted six-membered ring being considerably shorter. This trend is reproduced well by molecular mechanics calculations,[31, 33] that is, the very rigid bispidine type ligands are preorganized for tetragonal geometries, for example, for compounds that are stabilized by Jahn–Teller elongations. An ORTEP[34] diagram of the molecular cation of $[Cu(L^1)(Cl)]^+$ is shown in Figure 1. The copper(II) chromophore has a distorted square-pyramidal geometry; the distortion is expressed by the geometric parameter $\tau = 0.11$ ($\tau = 1$ for D_{3h} and $\tau = 0$ for C_{4v}).[35] The bond distances in the $CuNpy_2Cl$ basal plane are as expected ($Cu-N_{amine} = 2.04$ Å, $Cu-N_{pyridine} = 2.02$ Å, $Cu-Cl = 2.23$ Å), and the $Cu-N_{amine}$ distance to the apical donor is 2.27 Å.

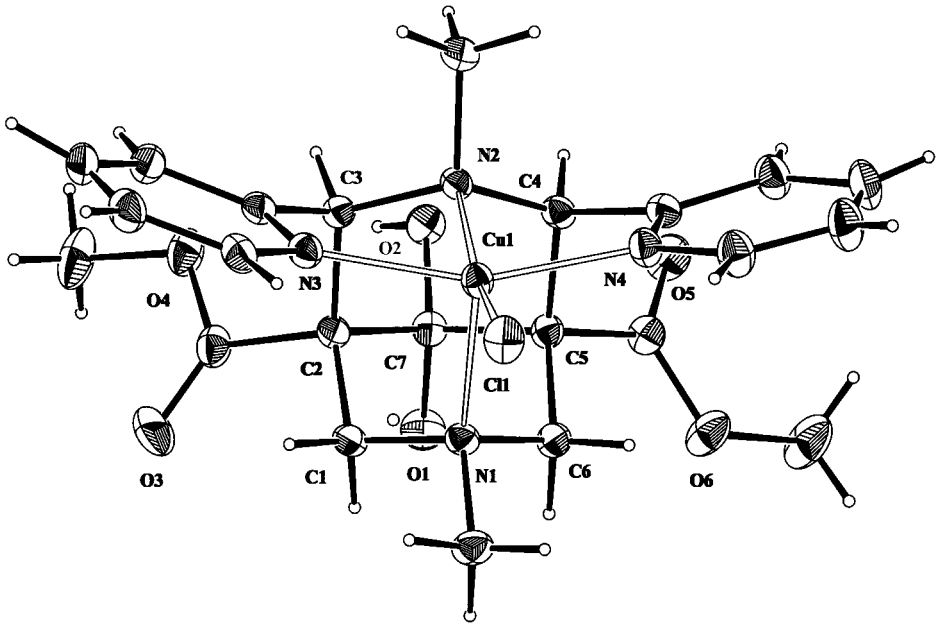

Figure 1. ORTEP[34] plot of the molecular cation of $[CuL^1Cl]Cl$ (bond lengths in Å, angles in °): Cu1–N1 = 2.2725 (0.0025) , Cul–N2 = 2.0423 (0.0025), Cu1–N3 = 2.0240 (0.0025), Cu1–N4 = 2.0204 (0.0025), Cu1–Cl1 = 2.2320 (0.0013), N2–Cu1–Cl1 = 165.02 (0.07), N3–Cu1–N4 = 158.13 (0.10), N2–Cu1–N1 = 85.03 (0.09), N3–Cu1–N1 = 95.36 (0.10), N4–Cu1–N1 = 95.96 (0.10), Cl1–Cu1–N1 = 109.95 (0.07).

The observed and computed structural features of $[M(L^1)X_n]^{m+}$ compounds ($n = 1,2$)[29–33] indicate that substrate binding (peroxide in the present case) might occur preferentially in the basal plane, that is, the copper–oxygen bond should be comparably short and strong. Note that this is a coordination mode that is different from that generally observed for (μ-peroxo)dicopper(II) compounds, in which trigonal bipyramidal structures predominate.[3, 5] Thus, the rigid bispidine ligand backbone is expected here to enforce a comparably stable copper(II)-peroxide bond. Also, the rather inflexible ligand cavity is not well suited for copper(I) coordination and it therefore is expected to lead to rather unstable, that is, highly reactive, copper(I) compounds. Note also that the differences in the copper(II)-peroxide bonding might lead to significant spectroscopic differences (vide infra).

The relative stability of the (μ-peroxo)dicopper(II) compound of L^1 was assessed with force field calculations. All starting structures refined without constraints to distorted square-based pyramidal structures. Owing to the rigidity of the bispidine backbone there are only a few isomers, and these were all refined; the peroxo bridge may be *trans* to the amine of the pyridine-substituted six-membered ring (N2 in the

Abstract in German: *Die Oxygenierung des Kupfer(I) Komplexes mit dem starren tetradentaten Liganden L^1, der ein Bispidin-Grundgerüst mit zwei Pyridyl-Seitenketten aufweist (L^1 = Methyl 2,4-bis(2-pyridinyl)-3,7-diazabicyclo-[3.3.1]-nonan-9-diol-1,5-dicarboxylat) produziert einen end-on (μ-peroxo)dikupfer(II) Komplex, der in Acetonitril bis zu 250 K stabil ist. Aus der spektroskopischen Analyse (UV/Vis, Raman) und einer Röntgenstrukturanalyse des vergleichbaren mononuklearen Kupfer(II) Komplexes $[Cu(L^1)Cl]^+$ folgt, dass das tief violette Oxygenierungsprodukt zwei verzerrt quadratisch pyramidale Kupfer(II) Chromophore aufweist, die durch eine μ-Peroxobrücke verbunden sind. Kraftfeldrechnungen werden verwendet, um die Stabilität von $[\{Cu(L^1)\}_2O_2]^{2+}$ zu interpretieren und einen Liganden L^2 zu entwerfen, bei dem zwei L^1-Einheiten durch eine Ethylbrücke verbunden sind. Das aus $[CuL^2]^+$ und Sauerstoff resultierende Dikupfer(II) Peroxoprodukt hat spektroskopisch (UV-vis, Raman) ähnliche, aber nicht identische Charakteristiken wie die Verbindung mit L^1. Das Oxygenierungsprodukt $[Cu_2(L^2)(O_2)]^{2+}$ ist stabil bei Raumtemperatur ($t_{1/2}$(298 K) = 50 min).*

X-ray structure of the mononuclear compound, see Figure 1) or *trans* to N1. A number of conformational isomers arise by torsions around the copper–oxygen and the oxygen–oxygen bonds. The four major isomers have a *trans* configuration of the μ-peroxo bridge and strain energies within a range of 5 kJ mol^{-1}; all other isomers are destabilized by at least 35 kJ mol^{-1}. When Jahn–Teller distortions were included in the model calculations there was, as expected (see above), a small but significant preference for the isomers with the peroxo bridge *trans* to the amine of the pyridine-substituted six-membered ring (N2 in Figure 1). The structure of the most stable isomer is shown in Figure 2.

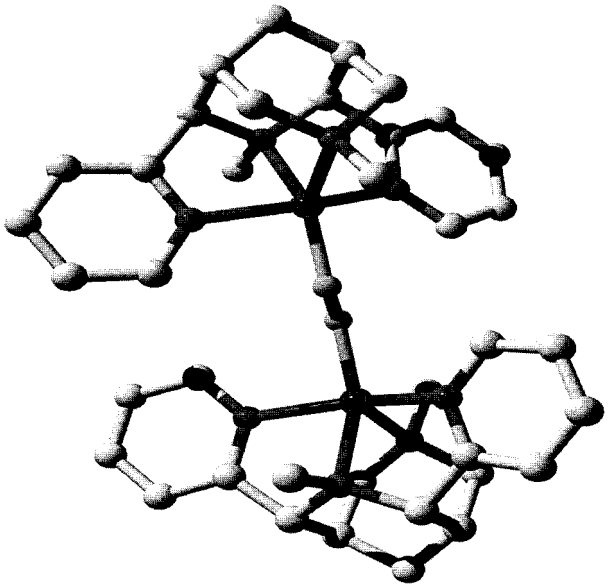

Figure 2. Plot of the computed structure of the most stable isomer of $[\{Cu(L^1)\}_2O_2]^+$.

From the computed structure and strain energy it emerges that:

1) The copper(II) chromophores are very similar to that of the experimentally determined mononuclear copper(II) species (Figure 1); the most prominent difference is a small but significant distortion towards a trigonal bipyramidal geometry ($\tau \sim 0.2$ vs. $\tau \sim 0.1$). Probably more relevant is the fact that in all low-energy structures the copper(II) centers are above the basal plane, and for the most stable calculated structure the *trans* angle between the peroxo bridge, the copper center, and the amine nitrogen of the pyridine-substituted six-membered ring is approximately 150°.
2) The peroxo bridge is somewhat shielded by the pyridine rings.
3) The double of the steric energy of a mononuclear $[Cu^{II}(L^1)O]$ fragment is larger than the strain energy of the most stable isomers of the μ-peroxo product. This latter effect is due to van der Waals attraction involving the pyridine groups.

All these steric factors, together with the rigid cavity of L^1 which is well suited for copper(II) (see also electronic factors, discussed qualitatively above), are responsible for the stabilization of the (μ-peroxo)dicopper(II) product (see below for experimental verification).

In order to further increase the stability of the oxygenation product the two bonding cavities of the ligand may be linked (preorganization of the dicopper(I) active site), and the optimum spacer group may be designed by molecular mechanics.[26] For preparative and also for steric reasons a bridge between the two amine donors of the unsubstituted six-membered ring (N1 in Figure 1) was prefered, and from the modeling studies it emerges that an ethyl spacer is most appropriate (L^2). The corresponding lowest energy (μ-peroxo)-dicopper(II) product is shown in Figure 3. The two chromophores are square pyramidal with $\tau \sim 0.1$). More importantly,

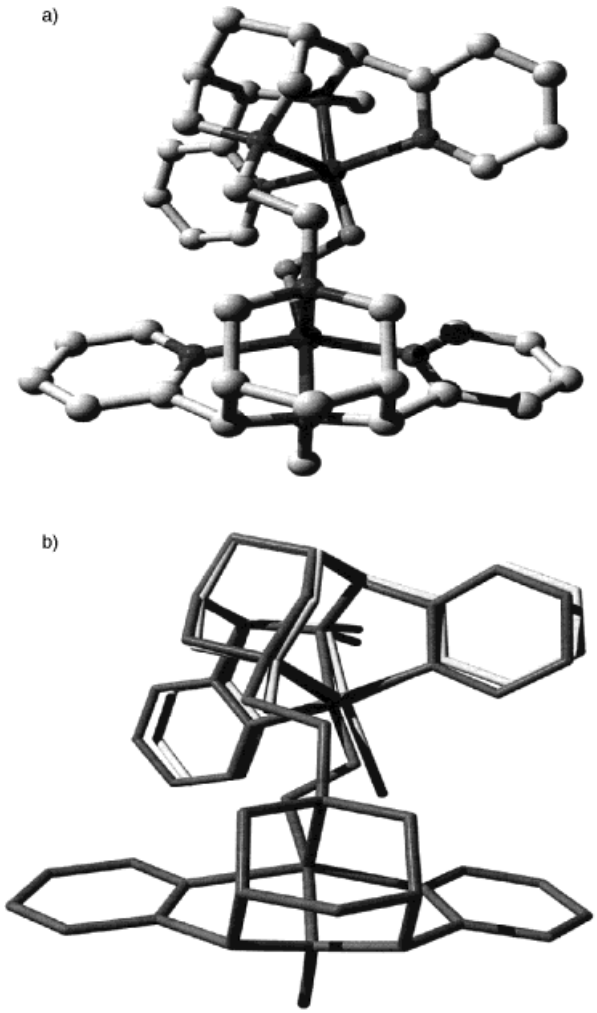

Figure 3. a) Plot of the computed structure of $[Cu_2L^2O_2]^+$; b) RMS overlay of the structures in Figures 1 and 3a.

the angle between the peroxo bridge, the copper(II) center, and the amine nitrogen of the pyridine-substituted six-membered ring is approximately 170°. Note again, that our molecular-mechanics model does not involve any predetermined coordination geometry.[26, 36] Also shown in Figure 3 is an RMS overlay with the experimentally determined structure of the mononuclear compound. This indicates that L^2 is well preorganized for the oxygenation reaction. It appears that the ethyl bridge helps to enforce a square-pyramidal

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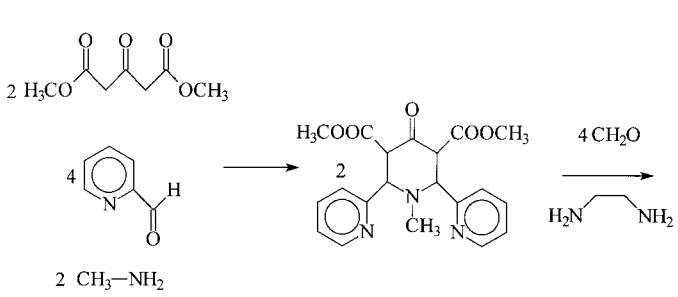
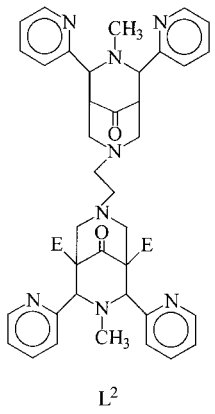
geometry, which might help to stabilize the peroxo bridge (vide supra). The strain energies of the core structures (substitution of the ethyl bridge and of the two methyl substituents with protons) are within 10 kJ mol^{-1}, that is, the ethyl bridge does not lead to an unacceptable build-up of steric strain.

Ligand syntheses and oxygenation reactions: L^2 was obtained in high yield by a Mannich condensation from the piperidone percursor,[27, 37] 1,2-diaminoethane and formaldehyde (Scheme 2), that is, this ligand and a range of possible derivatives with a large variety of spacer groups are easily available in relatively large quantities.





L^2

Scheme 2. Reaction scheme for the formation of L^2.

Oxygenation of $[Cu(L^1)(CH_3CN)](BF_4)$ in dichloromethane or acetonitrile at 193 K immediately yields a deep purple solution. The electronic spectroscopic data ($\lambda_1 =$ 520 nm, $\lambda_2 = 630$ nm (shoulder), acetonitrile, 233 K) and the Raman spectrum ($\tilde{\nu}(0\text{–}0) = 840$ cm^{-1}) are typical for a (μ-peroxo)dicopper(II) complex.[1, 25, 38, 39] This compound decays above approximately 250 K ($t_{1/2} \approx 15$ s). Formation and decay of the oxygenation product is reversible. The relatively high stability of the (μ-peroxo)dicopper(II) product[5] is attributed to i) the instability of the copper(I) precursor compound, ii) some electronic stabilization of the (μ-peroxo)dicopper(II) product owing to the distorted square-pyramidal geometry, and iii) a comparably low steric energy of the product. When dissolving $[Cu(L^1)(CH_3CN)]X$ ($X = OSO_2CF_3$, BF_4) in CH_2Cl_2 at room temperature, chloride abstraction from CH_2Cl_2 takes place and leads to the corresponding copper(II) compound $[Cu(L^1)Cl]^+$, with structural features similar to that described above.[32]

The spectroscopic properties of the copper oxygenation product of the dinucleating ligand, $[Cu_2(L^2)(O_2)]^{2+}$, are similar but not identical to those of $[\{Cu(L^1)\}_2O_2]^{2+}$ (see above and Figure 4), and there is a striking difference in terms of the thermal stability ($t_{1/2}(250\text{ K}) \approx 15$ s versus $t_{1/2}(298\text{ K}) \approx$ 50 min). Thus, as predicted by the force-field calculations, L^2 is well preorganized for the dicopper oxygenation product, and it produces one of the most stable (μ-peroxo)dicopper(II) products known so far. The shift of the major charge-transfer transition by 970 cm^{-1} towards higher energy suggests a subtle change in electronic structure that also leads to a weakening of the O–O bond (shift of the corresponding Raman transition from 840 cm^{-1} to 827 cm^{-1}). Based on the computed structures and those known for similar species,[5, 26] we assume that part of the stability and the spectroscopic changes may be due to the fact that the copper(II) chromophores are square pyramidal with peroxide bound in the square plane. A thorough study of the electronic properties and of the kinetics of the two systems discussed here are subject to further studies.

Experimental Section

Measurements: ^{1}H and ^{13}C NMR spectra at 200.13 and 50.54 MHz, were measured with a Bruker AS 200 spectrometer in $CDCl_3$ or CD_3CN with TMS as internal standard. ^{1}H and ^{13}C NMR spectra at 300 MHz and 75 MHz were measured on a General Electric QE-300 spectrometer. UV/Vis spectra were recorded with a Cary 1E or Cary 2300 instrument; elemental analyses were obtained from the microanalytical laboratory of the chemical institutes of the University of Heidelberg. Mass spectra (FAB) were measured on a Finnigan 8400 mass spectrometer. Raman spectra were obtained with a Spectra Physics 2085 Beamlock Ar Laser ($\lambda = 514.5$ nm; resonance Raman) or a Nd YAG laser ($\lambda = 1064$ nm; FT-IR Raman, 250–800 mW).

X-ray structure analysis: Monoclinic crystals, space group: C2/c, $a =$ 18.702(9), $b = 13.644(7)$, $c = 22.614(11)$ Å, $\beta = 96.93(3)^\circ$, $V = 5728(5)$ Å^3, $Z = 8$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), ω scan, $-70\,^\circ$C, $2\theta_{max} = 54^\circ$, 6260 independent reflexes (4742 observed with $I \geq 2\sigma_I$), empirical absorption correction. Structure determination with direct methods (SHELXS86), refinement with all observed reflexes against F^2 (SHELXL97), non-H atoms anisotropic, H atoms isotropic, $R1 = 0.04$, $wR2 = 0.12$, rest electron density $= +0.8$ eÅ^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-113633. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Molecular mechanics: The MOMEC suite of programs[36] and the force field[40] were used for molecular mechanics calculations. The approach used for modeling the (μ-peroxo)dicopper(II) compounds has been published elsewhere[26] and the only modification to the force field was that of the bond-stretching parameter set to the apical nitrogen donor (Cu1–N1 in Figure 1; $k_b = 0.3$ mdyn Å^{-1}; $r^0 = 2.05$ Å). This model for the Jahn–Teller elongation of this bond is based on an approach that has been described before;[40] the parameter set was validated with the experimental structure of $[Cu(L^1)(Cl)]^+$ (Figure 1). The force field used is based on a points-on-a-sphere model, in which the angular geometry around the metal center is determined by 1,3-nonbonded interactions alone,[40] that is, there are no constraints in terms of the coordination geometry.

Ligand syntheses: L^1 and the piperidone precursors were prepared by published procedures.[27, 37] L^2: A 37% aqueous HCHO solution (1.82 mL, 20.2 mmol) and aqueous 1,2-diaminoethane (0.41 mL, 5 mmol) were added to a solution of the piperidone (3.22 g, 8.41 mmol) in THF (20 mL) at room temperature. The resulting white suspension was refluxed for 1 h. Slow evaporation of the solvent at room temperature led to a black tarlike residue. Stirring in MeOH (5 mL) led to the formation of white precipitate, which was filtered off, washed twice with cold EtOH, and dried in high vaccum. Yield: 3.3g (3.7 mmol, 88%); ^{1}H NMR (200 MHz, $CDCl_3$):

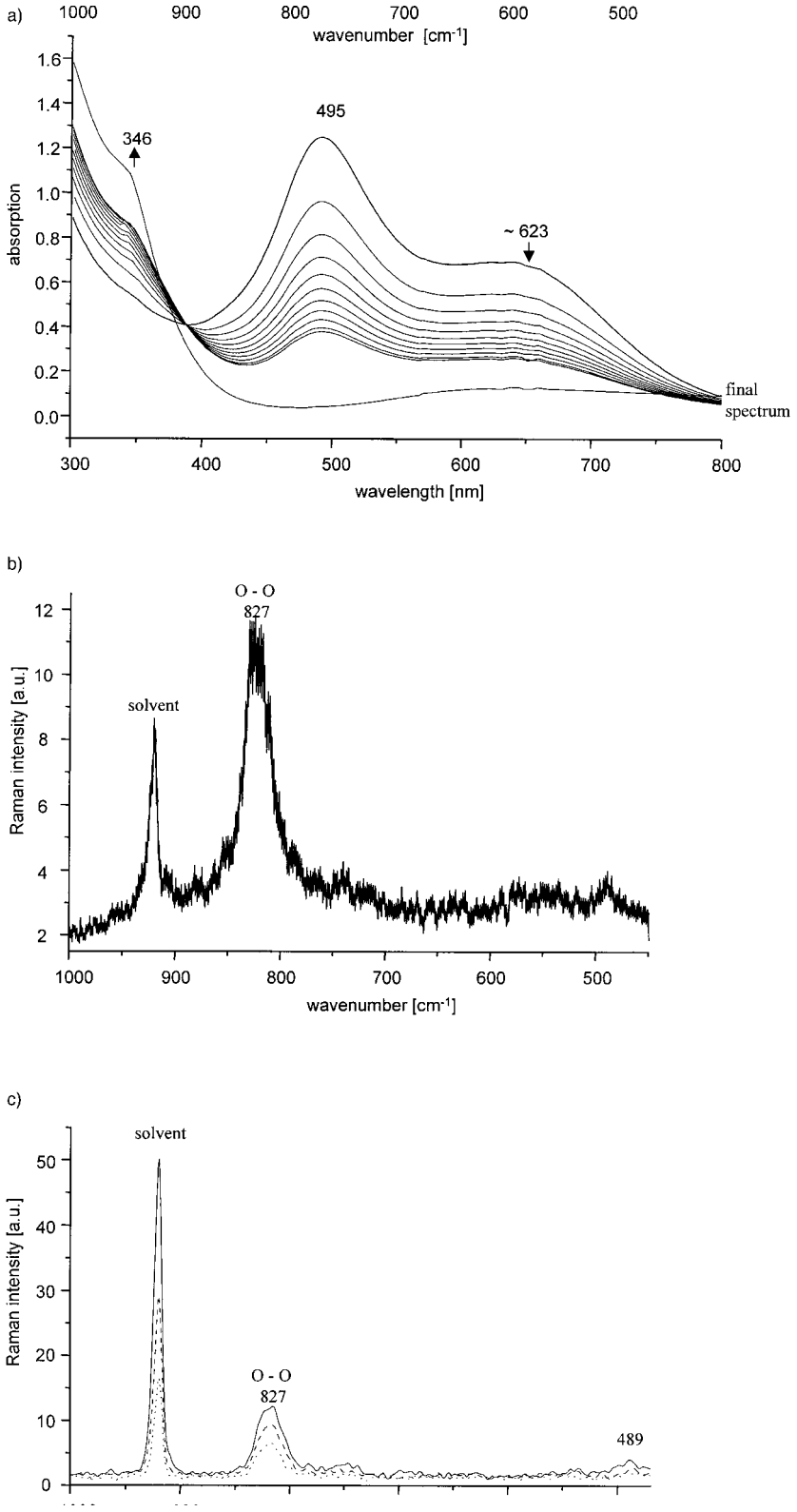


Figure 4. a) UV/Vis spectra of $[Cu_2L^2O_2]$ (solvent: CH_3CN). Spectra at 298 K were recorded every 10 minutes; (Cu^+:L^2:O_2 = 2:1:1); $\varepsilon_{495} = 7900$, $\varepsilon_{623} = 5400$ L mol^{-1} cm^{-1}. b) Resonance Raman spectrum of $[Cu_2L^2O_2]^{2+}$ in CH_3CN; for excitation the green line ($\lambda = 514.4$ nm) of an argon ion laser (Spectra Physics, model 2085 Beamlok) was used. c) FT-IR Raman spectra of $[Cu_2L^2O_2]^{2+}$. Nd:YAG laser operating at 1064 nm with a power of 800 mW (—), 500 mW (- - -), 250 mW (· · ·).

$\delta = 2.05$ (s, 6H; N−CH_3), 2.44 (s, 4H; $CH_{2,en}$), 2.61(d, ^2J(H,H) = 12 Hz, 4H; bis $CH_{2,ax}$−N), 2.99 (d, ^2J(H,H) = 12 Hz, 4H; bis $CH_{2,eq\text{-}N}$), 3.86 (s, 6H; CO_2−Me), 4.74 (s, 4H; CH−Py), 7.21 (m, 4H; $H5_{py}$), 7.65 (t, 4H; $H4_{py}$), 7.96 (d, 4H; $H3_{py}$), 8.51 (d, 4H; $H6_{py}$); ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 42.95$ (N−CH_3), 52.25 (O−CH_3), 54.71 ($CH_{2,en}$), 58.95 (CH_2−N), 62.00 (C_{quart}), 73.26 (C−Py), 122.76, 123.19, 135.99, 148.50, 158.37 (C_{py}), 168.39 (COOMe), 203.05 (C=O); FAB-MS: 875 (100%, $[M+H]^+$); $C_{46}H_{50}N_8O_{10}\cdot H_2O$ (892): calcd C 61.88, H 5.83, N 12.56%; found C 61.28, H 5.91, N 12.29%.

$[Cu(L^1)(CH_3CN)]BF_4$: $[Cu(CH_3CN)_4]BF_4$[41] (0.5 g, 1.6 mmol) in CH_3CN (10 mL) was added slowly under Ar to a suspension of L^1 (0.7 g, 1.6 mmol) in CH_3CN (4 mL). The clear yellow-orange solution was evaporated to dryness to yield the yellow-brown product as an air-sensitive powder (1.0 g, 1.59 mmol, 99%). ^{1}H NMR (200.13 MHz, CD_3CN): $\delta = 8.70$ (br, 2H; $CH6_{py}$), 7.90 (t, $^3J_o = 7.3$ Hz, 2H; $CH4_{py}$), 7.51 (br, 2H; $CH3_{py}$), 7.30 (br, 2H; $CH5_{py}$), 4.90 (br s, 2H; bis CH2, CH4), 3.73 (s, 6H; OCH_3), 3.15 (d, 2H; bis $CH6_{eq}$, $CH8_{eq}$), 2.81 (d, 2H; bis $CH6_{ax}$, $CH8_{ax}$), 2.49 (s, 3H; N3−CH_3), 2.12 (s, 3H; N7−CH_3); ^{13}C{^{1}H} NMR (50.13 MHz, CD_3CN): $\delta = 201.8$ (s, bis-C9), 167.8 (s, C=O ester), 154.9 (br s, $C2_{py}$), 150.4 (br s, $C6_{py}$), 139.6 (s, $C4_{py}$), 126.1 (br s, $C5_{py}$, $C3_{py}$), 71.5 (br s, bis C2, C4), 62.6 (s, bis C1, C5), 61.8 (s, bis C6, C8), 53.8 (s, OCH_3), 49.1 (s, N3−CH_3), 44.3 (s, N7−CH_3); IR (KBr): $\tilde{\nu} = 3500-3000$ (w, C_{py}–H), 2972 (m, CH_2), 2879 (w, OC−H), 1755 (s, C=O, ester), 1739 (s, C=O, ketone), 1600 (m, C=N_{py}), 1440 (m, CH_2), 1288, 1273 (s, C−OCH_3), 1061 (s, B−F_4), 792 (s, C_{ar}–H); $C_{25}H_{29}N_5O_5CuBF_4$ (629.88): calcd C 47.67, H 4.64, N 11.12; found C 47.15, H 4.65, N 10.65.

$[Cu_2(L^2)(CH_3CN)_2]^{2+}$: $[Cu(CH_3CN)_4]BF_4$[41] (72 mg, 0.23 mmol) or $[Cu(CH_3CN)_4]SO_3CF_3$[42] (86 mg, 0.23 mmol) in CH_3CN (1 mL) was added under N_2 to a suspension of L^1 (100 mg, 0.115 mmol) in CH_3CN (1 mL). The clear yellow-orange solution was put in a ether-diffusion bath to prompt precipitation of the yellow product. ^{1}H NMR (300 MHz, CD_3CN, $[Cu_2(L^2)](SO_3CF_3)_2$): $\delta = 1.89$ (s, 6H; N−Me), 3.01 (d, $^2J = 12$ Hz, 4H), 3.15 (s, 4H; $CH2_{en}$), 3.59 (d, $^2J = 12$ Hz, 4H), 3.79 (s, 12H; COOMe), 4.88 (s, 4H; CH−Py), 7.36 (d, $^2J = 6$ Hz, $CH5_{py}$), 7.54 (t, $CH3_{py}$), 7.92 (t, $CH4_{py}$), 8.7 (d, $^2J = 3$ Hz; $CH6_{py}$); ^{13}C NMR (75 MHz, CD_3CN): $\delta = 43.66$ (N3−CH_3), 52.78 (OCH_3), 57.29 (C6, C8), 59.39 ($CH2_{en}$), 61.66 (C1, C5), 70.91 (C2, C4), 125.29, 138.6, 149.47, 153.82 (all C_{py}), 166.64 (COOMe), 200.2 (C9); $[Cu_2(L^2)(CH_3CN)_2](SO_3CF_3)_2$: $C_{52}H_{56}O_{16}N_{10}Cu_2S_2F_6$ (1382.28): C 45.18, H 4.08, N 10.13; found C 45.10, H 4.22, N 10.01; $[Cu_2(L^2)(CH_3CN)_2](BF_4)_2$: $C_{50}H_{56}O_{10}N_{10}Cu_2B_2F_8$ (1257.75): C 47.75, H 4.49, N 11.14; found C 47.48, H 4.49, N 11.02.

(μ-Peroxo)dicopper(II) compounds: Solutions of the (μ-peroxo)dicopper(II) compounds $[\{Cu_2(L^1)\}_2O_2]^{2+}$ and $[Cu(L^2)(O_2)]^{2+}$ were obtained by bubbling dry O_2 for 2 minutes through 5 mL of a 10 mmol solution of the corresponding Cu(I) complexes in dry degassed CH_3CN.

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