

(*N*-Benzyl-bis-*N'*,*N''*-salicylidene)-*cis*-1,3,5-triaminocyclohexane copper(II): a novel catalyst for the aerobic oxidation of benzyl alcohol

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Reaction of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ with the N_3O_2 donor ligand H_2L (where $\text{H}_2\text{L} = N$ -benzyl-*N'*,*N''*-di-*tert*-butyl-disalicyl-triaminocyclohexane) results in the formation of a novel $\text{Cu}^{\text{II}}\text{L}$ complex, **1**. X-Ray crystallography of **1** shows the Cu^{II} centre coordinated by two phenolate oxygens and two imine nitrogens in a distorted square plane with an elongated bond to the amine nitrogen (2.512 Å) in the axial position. EPR spectroscopy of **1** gives g values of $g_1 = 2.277$, $g_2 = 2.100$, $g_3 = 2.025$, and $A_1 = 15.6$ mT which are consistent with the distorted square pyramidal coordination environment determined from the X-ray structure. UV/visible and electrochemical analysis of **1** shows that it undergoes two reversible processes assigned to the successive oxidation of the phenolate oxygens to phenoxyl radicals, the first at $E_{1/2} = 0.89$ V ($\Delta E = 81$ mV, vs. Ag/AgCl) and the second at $E_{1/2} = 1.13$ V ($\Delta E = 84$ mV, vs. Ag/AgCl). Chemical oxidation of **1** results in the formation of a species, assigned as $[\text{1}]^{\bullet+}$ which is EPR silent due to antiferromagnetic coupling between the Cu^{II} centre and the bound phenoxyl radical. The oxidised species catalyses the oxidation of benzyl alcohol to benzaldehyde.

Introduction

The fungal enzyme *galactose oxidase* (GOase)^{1,2} catalyses the selective oxidation of primary alcohols to aldehydes with the concomitant reduction of O_2 to H_2O_2 .³ The overall oxidation process requires two electrons and the enzyme does this with the use of both a $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ and a tyrosyl/tyrosinate redox couple.^{4,5} In recent years there has been considerable focus on the preparation of small molecule models of the active site of GOase.^{6,7} These complexes are of inherent interest as potential catalysts for selective oxidation chemistry.

We have previously prepared and studied a range of coordinatively saturated Fe^{III} complexes prepared from N_3O_3 donor ligands based on salicyl derivatives of 1,3,5-*cis,cis*-triaminocyclohexane ligands.⁸ The Fe^{III} complexes exhibit reversible ligand-based oxidation processes to give bound phenoxyl radical species at remarkably low oxidation potentials. The complexes are, however, coordinatively saturated at the metal centre, limiting their ability to act as oxidation catalysts. We have now developed this ligand system further with the preparation of a novel unsymmetrical 1-amino-3,5-diiminocyclohexane-based N_3O_2 ligand.⁹ Our objective is to couple the stable ligand-based redox properties with a redox-active coordinatively unsaturated metal site (as in GOase), thus providing a novel chemical system capable of oxidation catalysis. Herein we describe the preparation and characterisation of a copper complex using this ligand system, including the EPR, X-ray structure, UV/visible studies, chemical oxidation and catalytic studies. We show that the complex catalyses the oxidation of benzyl

alcohol to benzaldehyde. Such catalytic behaviour suggests that the complex offers the potential to act as an effective oxidation catalyst in other reactions.

Results and discussion

Preparation of the novel N_3O_2 donor ligand is carried out by a simple Schiff base condensation reaction of two equivalents of a 3,5-derivatised salicylaldehyde (to give the phenolate moiety) with the novel primary amine, **I**, to give the ligand H_2L (*N*-benzyl-*N'*,*N''*-di-*tert*-butyl-disalicyl-triaminocyclohexane, Fig. 1). Derivatisation in these positions of the phenolate group has been shown to enhance the stability of any subsequent radical species.^{8,10} Complexation of the H_2L ligand with $\text{Cu}^{\text{II}}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ occurs readily to give the corresponding $\text{Cu}^{\text{II}}\text{L}$ complex (**1**), in 70% yield (Fig. 1). **1** is purified by column chromatography on neutral alumina to give the product as a green complex which can be crystallised by slow evaporation of an alcohol solution of the complex.

The X-ray structure of **1** shows a five-coordinate copper(II) ion bound by two imine nitrogen atoms and the amine from the tach and two phenolate oxygen atoms giving a distorted square pyramidal coordination geometry (Fig. 2). The copper to imine nitrogen atom bond lengths [av. 1.991(4) Å] and the copper to phenolate oxygen atom bond lengths [1.936(3) Å and 1.994(4) Å] are within the expected ranges and provide the square base around the copper, the bond to the amine group [2.512(4) Å] is elongated and in the axial position. The sixth coordination site is unoccupied. Structurally characterised unsymmetrical tach complexes are limited to only a few examples.¹¹ **1** is the first example of a pentacoordinating tach-based ligand.

The EPR spectrum (77 K) of **1** was recorded in frozen CH_2Cl_2 solution (Fig. 3). Computer simulation of the spectrum gives

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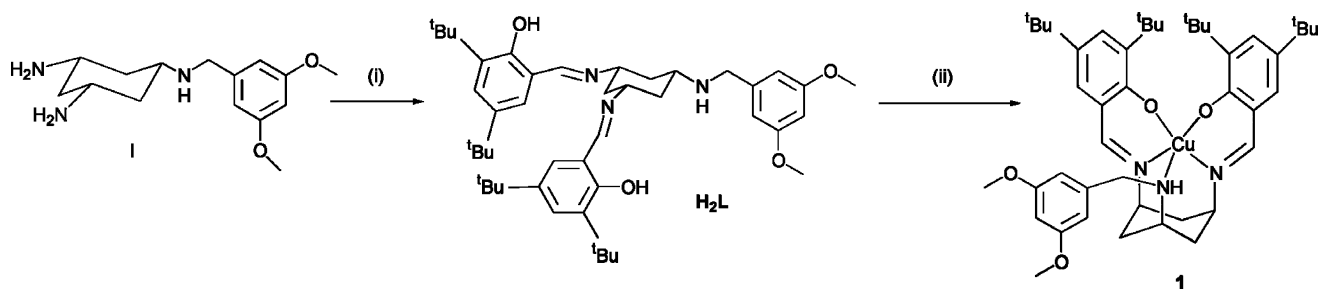


Fig. 1 Preparation of the N_3O_2 donor ligand and the corresponding $Cu^{II}L$ complex (**1**). Conditions: (i) 2 equivalents of 3,5-di-*t*-Bu-salicylaldehyde, MeOH; (ii) $Cu(BF_4)_2 \cdot 6H_2O$, MeOH.

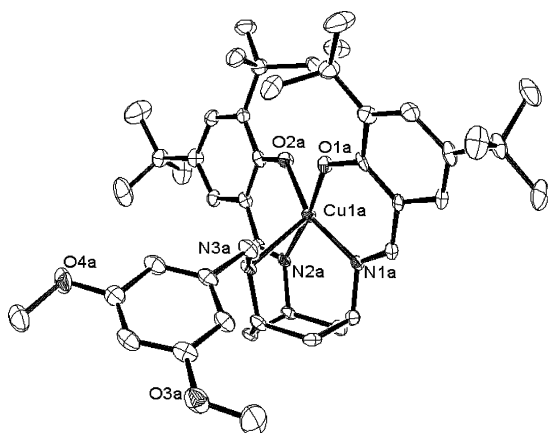


Fig. 2 ORTEP¹² view (50% probability ellipsoids) of the X-ray crystal structure of **1**. Selected bond lengths (Å) and angles (°): Cu(1A)–O(1A) 1.936(3), Cu(1A)–N(1A) 1.991(4), Cu(1A)–N(3A) 2.512(4), Cu(1A)–O(2A) 1.994(4), Cu(1A)–N(2A) 1.991(4); O(1A)–Cu(1A)–O(2A) 84.41(15), O(2A)–Cu(1A)–N(1A) 159.06(17), O(2A)–Cu(1A)–N(2A) 90.37(16), O(1A)–Cu(1A)–N(3A) 97.39(14), N(1A)–Cu(1A)–N(3A) 80.21(16), O(1A)–Cu(1A)–O(2A) 84.41(15), O(1A)–Cu(1A)–N(1A) 89.82(16), O(1A)–Cu(1A)–N(2A) 171.99(16), N(1A)–Cu(1A)–N(2A) 97.16(17), O(2A)–Cu(1A)–N(3A) 120.45(15), N(2A)–Cu(1A)–N(3A) 80.01(15).

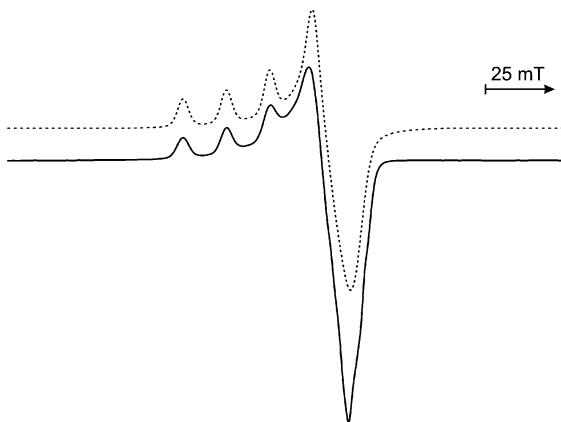


Fig. 3 Frozen solution EPR spectrum of **1** recorded at 77 K in CH_2Cl_2 (—) and simulated spectrum (·····).

parameters of $g_1 = 2.277$, $g_2 = 2.100$, $g_3 = 2.025$, and $A_1 = 15.6$ mT, values that are typical of a Cu^{II} centre coordinated by three nitrogens and two phenolate oxygens in a distorted square-

pyramidal environment $\{a(d_{x^2-y^2})^1$ electronic configuration $\}^{13-18}$. The results suggest that the solution structure of the complex is very similar to that found in the solid state structure. When recording the EPR spectrum of the complex, it was noted that the appearance of the spectrum changed when a coordinating solvent, such as methanol, was employed. This suggests that the Cu centre can accommodate a sixth ligand.

The UV/visible spectrum of **1** in CH_2Cl_2 (Fig. 4) shows five different bands, three of which (230, 258, 326 nm, $\epsilon = 6000$ to 170000 dm^3 mol^{-1} cm^{-1}) are assigned to ligand-based π to π^* charge transfer transitions (in reference to the free ligand). A fourth band at 378 nm is assigned to a LMCT transition from the phenolate to the Cu^{II} metal centre ($\epsilon = 628$ dm^3 mol^{-1} cm^{-1}).^{14,15,17} A fifth band at 594 nm ($\epsilon = 130$ dm^3 mol^{-1} cm^{-1}) is assigned to a metal-based transition.

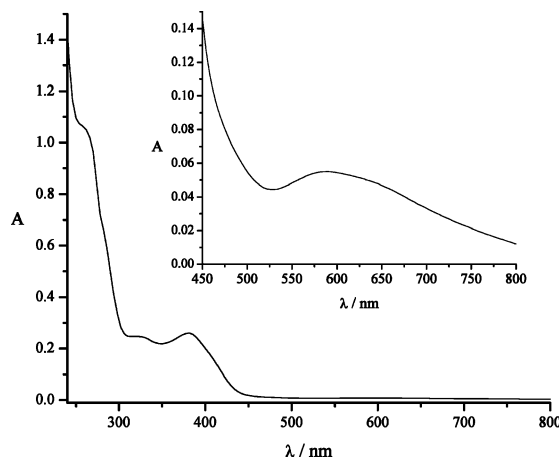


Fig. 4 UV/visible spectrum of a CH_2Cl_2 solution of **1** (4×10^{-5} mol dm^{-3}) recorded at room temperature (4×10^{-4} mol dm^{-3} inset).

The cyclic voltammogram (CV) of **1** in CH_2Cl_2 (Fig. 5); shows no electrochemical processes in the negative region (between 0 and -1.8 V vs. Ag/AgCl, not shown). Two reversible processes on the CV timescale are apparent at positive potentials; the first at $E_{1/2} = 0.89$ V ($\Delta E = 81$ mV, 0.34 V vs. $FeCp_2/FeCp_2^+$) and the second at $E_{1/2} = 1.13$ V ($\Delta E = 84$ mV, 0.58 V vs. $FeCp_2/FeCp_2^+$). These processes are observed at slightly lower potentials in MeCN, the first at $E_{1/2} = 0.80$ V ($\Delta E = 70$ mV, 0.33 V vs. $FeCp_2/FeCp_2^+$) and the second at $E_{1/2} = 1.03$ V ($\Delta E = 80$ mV, 0.56 V vs. $FeCp_2/FeCp_2^+$). Differential pulse experiments confirm that there is only one electron involved in each of the two processes.

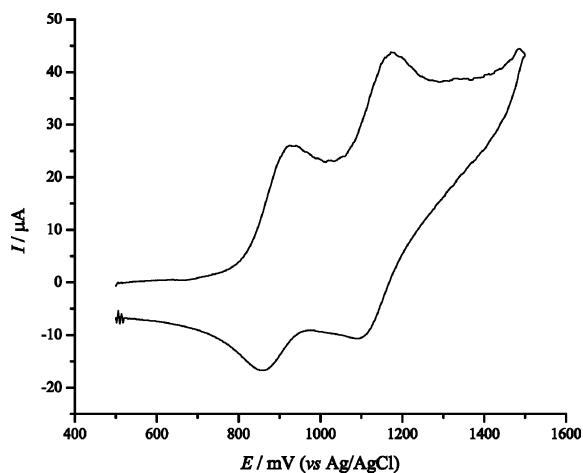


Fig. 5 Cyclic voltammogram (298 K) of **1** (1×10^{-4} mol dm $^{-3}$) in CH $_2$ Cl $_2$ solution (0.5 mol dm $^{-3}$ [NBu $_4$]BF $_4$) recorded at 200 mV s $^{-1}$.

In reference to previous phenolate–tach complexes,⁸ both the first and second reversible oxidation processes observed in the CV of **1** are assigned to the production of first one and then a second phenoxyl-radical. It appears, therefore, that **1** undergoes two reversible ligand-based, phenolate to phenoxyl-radical redox processes, and no metal-based processes are observed within the redox range of the experiment.^{14,15,17} Another example of this type of redox behaviour was observed with a N $_3$ O $_2$ triazaacyclononane-based system prepared by Tolman and co-workers.¹⁶ In this case, both the Zn II and Cu II complexes undergo analogous oxidation chemistry; the system also incorporates the same di-*tert*-butyl substitution pattern around the phenolate ring. Stack and co-workers also observed similar behaviour from a binaphthyl salen-type N $_2$ O $_2$ -donor Cu II complex.^{14,17}

The first oxidation process observed for **1** can be carried out chemically by addition of Cu II (CF $_3$ SO $_3$) $_2$ ($E_1 = 0.95$ V vs. Ag/AgCl in MeCN, 0.40 V vs. FeCp $_2$ /FeCp $_2^+$).¹⁹ When the oxidant is added to a dilute pale green MeCN solution of **1** an instantaneous colour change to intense dark emerald green is observed. The UV/visible spectrum of the dark emerald green solution of [1] $^{+}$ (Fig. 6) shows a strong absorption band at 390 nm

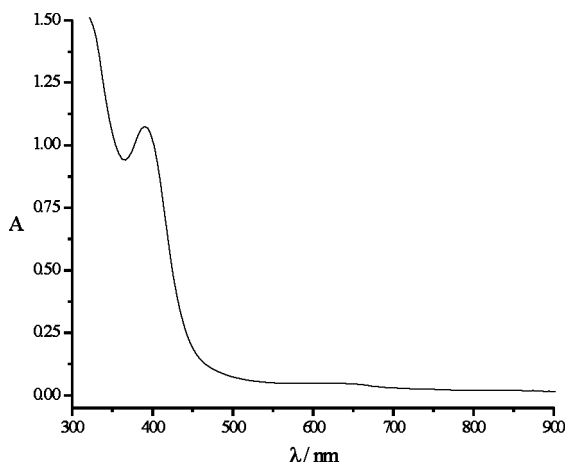


Fig. 6 UV/visible spectrum of a MeCN solution of the chemically generated [1] $^{+}$ species (1×10^{-4} mol dm $^{-3}$) recorded at room temperature.

($\epsilon = 9860$ dm 3 mol $^{-1}$ cm $^{-1}$) which is assigned to a phenoxyl-radical to Cu II LMCT⁸ in analogy to the electronic spectrum of the oxidised active form of GOase, which shows a distinctive feature at 445 nm ($\epsilon \approx 50\,000$ dm 3 mol $^{-1}$ cm $^{-1}$) likely to be due to a tyrosyl-radical to Cu II LMCT band.²⁰ Parallel EPR experiments on the oxidised [1] $^{+}$ complex show that the addition of the oxidant to the complex results in the complete loss of the EPR signal. This loss of EPR activity strongly suggests that the bound phenoxyl-radical species, which is produced when the complex is oxidised, is anti-ferromagnetically coupled to the Cu II centre.

We have completed a preliminary study into the aerobic oxidation of benzyl alcohol to benzaldehyde using **1** as the catalyst. We have followed the method used by Stack and co-workers so that the two catalytic systems can be compared directly.¹⁴ Approximately 4% of the substrate was added to the reaction mixture in the deprotonated form (as the sodium salt, PhCH $_2$ ONa). The oxidation reactions were initiated by the final addition of the chemical oxidant, Cu II (CF $_3$ SO $_3$) $_2$ (1 : 1 ratio to **1**), to all the other components. The reactions were then monitored from this point onwards by GC, the reactions were run in air at room temperature. Control reactions without the presence of the catalyst show that the chemical oxidant, Cu II (CF $_3$ SO $_3$) $_2$ can perform one pseudo-catalytic turnover. The amount of benzaldehyde produced by the Cu II (CF $_3$ SO $_3$) $_2$ complex alone was taken into account when the turnovers numbers for the oxidation reactions were calculated. Analysis of the products by gas chromatography confirm the oxidation of benzyl alcohol to benzaldehyde is catalysed by **1** [average of 44 turnovers in 24 h ($\sim 2\%$ of substrate), 160 turnovers in 144 h ($\sim 8\%$ of substrate) at 295 K]. Oxidation of benzyl alcohol is likely to occur on the coordinated alcoholate anion rather than directly on the alcohol itself. We note, however, that up to 8% of the substrate is oxidised, greater than the 4% of PhCH $_2$ ONa which is added to the reaction. This shows that whilst PhCH $_2$ ONa is necessary to allow coordination of the substrate to the complex, benzyl alcohol is the species which is the principal substrate for the oxidation reaction. Tests carried out in the absence of air show much reduced oxidation activity indicating that the oxidant of **1** to give the active [1] $^{+}$ species is molecular oxygen, although we cannot rule out the possibility that hydrogen peroxide—which may be produced as a product of the reaction—also plays an oxidative role.

There are several examples of oxidation catalysts based on GOase which aerobically oxidise primary alcohols to aldehydes. Copper complexes of thio-bis(2,4-di- i Bu-phenol), seleno-bis(2,4-di- i Bu-phenol), bis(2-hydroxy-3,5-di- i Bu-phenyl)amine and bis(2-hydroxy-3,5-di- i Bu-phenyl)phenylenediamine by Wieghardt and co-workers incorporate features seen in the active site of GOase, such as coordinated phenoxyl radicals, but all but the last are not direct structural models of the active site.^{6g,21} These complexes act as active catalysts for the aerobic oxidation of a range of different primary alcohols, the copper complexes which incorporate sulfur, however, also oxidise secondary alcohols and carry out oxidative C–C coupling reactions. The complexes incorporating selenium-based ligands show better selectivity, oxidising benzyl alcohol to benzaldehyde with 95 turnovers in 24 h.^{6g}

The activity of **1** is similar to the analogous bis(di-*tert*-butylsalicyl-imine)-binaphthyl Cu II complex described by Stack and co-workers which gives 40 turnovers in 20 h under the same conditions.¹⁴ A bis(2-hydroxy-3,5-di- i Bu-phenyl)ethylene-diamine

copper complex, prepared by Pierre and co-workers, has been evaluated for the catalytic oxidation of primary alcohols ROH to RCHO (where R is Me, Et, Pr and Bu).²² The complex is selective for the aerobic oxidation of primary alcohols and is reported to give a maximum number of turnovers of 30. Later work by the same group showed that the copper complex of an unsymmetrical pyridyl-bis(2-hydroxy-3-*t*-Bu-phenyl)amine ligand catalyses the oxidation of benzylalcohol with approximately 300 turnovers in 24 h.^{6d}

1 compares favourably with existing aerobic catalysts, and—compared to others—**1** is notable for its longevity under catalytic conditions. Future work will concentrate on the development of this ligand system and the application of the complexes as catalysts in a wide range of oxidation processes.

Conclusions

We have demonstrated the design and synthesis of a new Cu(II) complex of a N₃O₂ donor ligand based on a bis-salicyl derivative of *cis,cis*-1,3,5-triaminocyclohexane, using a new synthetic method to prepare the unsymmetrical ligands. We suggest that this complex exhibits reversible redox chemistry involving the successive oxidation of the two coordinated phenolate groups to give two bound phenoxyl radicals. The complex has also been found to be an active catalyst and is effective for the oxidation of benzyl alcohol to benzaldehyde.

Experimental

General procedures

Solvents for synthesis were supplied by Fisons Ltd., or Fischer Scientific International Company. Deuterated solvents were supplied by Aldrich Chemical company and Goss Scientific. All other reagents were supplied by either Aldrich Chemical Company Ltd., Lancaster Chemicals Ltd., Avocado Research Chemicals Ltd. or Fluka Ltd. All the reagents were used without further purification unless stated otherwise. FT-NMR spectra were recorded using a JEOL EX270 MHz spectrometer, referencing of the peaks was carried out using the residual protons in the solvent. Infrared spectra were recorded using a Mattson Sirius Research Series FTIR Spectrometer as KBr discs (pressed under 7 tonnes pressure). The data obtained were processed using Microsoft Win 1st software. Mass spectra were recorded on a Fisons Instruments Autospec. using a 0 to 650 °C temperature range. Elemental analyses were performed at the micro analytical laboratory at the University of Manchester. EPR spectra were recorded on a JEOL JES-RE1X Spectrometer (equipped with an X-band Gunn diode). Low temperature spectra were recorded with the use of a liquid N₂ dewar (at 77 K). UV/visible spectra were recorded on a Hitachi U-3000 spectrometer using 1 cm³ quartz cells.

Cyclic voltammetry was performed using a standard three-electrode configuration with platinum working (0.5 mm diameter disk) and counter electrodes and a Ag/AgCl reference which gave the FeCp/FeCp⁺ couple at 0.55 V ($\Delta E = 80$ mV) using an EG & G potentiostat. All measurements were made in a nitrogen-purged solution of either CH₂Cl₂/0.5 mol dm⁻³ [*n*-Bu₄N][BF₄] or MeCN/0.2 mol dm⁻³ [*n*-Bu₄N][BF₄], over a range of scan rates (from 50 to 500 mV).

Synthesis

Preparation of 1. H₂L (70.1 mg, 0.10 mmol, 1.00 equiv) was dissolved in MeOH (10 mL) to give an orange solution. Cu^{II}(BF₄)₂·6H₂O (34.7 mg, 0.10 mmol, 1.00 equiv) was dissolved in MeOH (10 mL) to give a very pale blue solution. The two solutions were added together and an instantaneous colour change to dark green was observed, the solution was then left to stir for 18 h. The solution was filtered and then evaporated to dryness to yield a dark green glassy solid which was further dried under vacuum (53.2 mg, 70%, 0.07 mmol). The complex can be purified by column chromatography on neutral alumina (product *R_f* = 0.60 in CH₃OH) to give **1** as green crystals. Elemental analysis: C₄₅H₆₃N₃O₄Cu: calc C 69.87, H 8.21, N 5.43, found C 69.44, H 8.03, N 5.06%. MS (ES): *m/z* = 773 (M⁺ [⁶³Cu]), 775 (M⁺ [⁶⁵Cu]). IR/cm⁻¹ (KBr pressed disk): 3438 (m, b), 3201 (w), 2958 (s), 2907 (m), 2870 (m), 1645 (m), 1613 (s, -CH=N-), 1533 (w), 1466 (m), 1417 (m), 1362 (m), 1254 (w), 1207 (m), 1156 (s), 1069 (s), 839 (w), 770 (w), 739 (w).

Crystallography

Crystals of Cu^{II}L were grown by slow evaporation of a propan-2-ol solution of the complex. The X-ray diffraction data were measured at Station 9.8 of the CCLRC Daresbury Laboratory Synchrotron Radiation Source using a Bruker AXS SMART CCD diffractometer, ω rotation with narrow frames (synchrotron radiation, $\lambda = 0.6883$ Å). Crystal structure analysis for (Cu^{II}L): C₄₈H₇₀CuN₃O₅, *M* = 832.61, green plates, crystal dimensions 0.07 × 0.06 × 0.02 mm, triclinic, *a* = 13.2972(12), *b* = 15.5508(14), *c* = 23.798(2) Å, $\alpha = 99.359(2)^\circ$, $\beta = 102.082(2)^\circ$, $\gamma = 104.520(2)^\circ$, cell volume = 4536.4(7) Å³, *T* = 150(2) K, space group *P* $\bar{1}$, *Z* = 4, 34089 reflections collected, 12962 unique, *R*_{int} = 0.0806. The structure was solved using direct-methods in SHELXS and refined using SHELXL, *R*₁ = 0.0621 (for 8884 reflections with *I* > 2σ(*I*)), *wR*₂ = 0.1684 (all data).

CCDC reference number 282729.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512296c

Oxidation chemistry

The catalytic oxidation reactions were carried out in air using 2 mL of MeCN as a solvent at room temperature. 1,2-Dichlorobenzene was used as an internal standard. In each experiment to 100% of PhCH₂OH (1.94 mol dm⁻³) there was 0.05% of **1** (0.97 mmol dm⁻³) [and 0.05% of the initiator Cu^{II}(CF₃SO₃)₂], 4% of PhCH₂ONa and 5% of 1,2-dichlorobenzene present. 20 μL aliquots of the reaction were removed after 2, 24, 48, 72 and 144 h and then quenched with 20 μL of Et₂O. These small samples were then analysed by GC. Control reactions without the presence of the catalyst show that the chemical oxidant, Cu^{II}(CF₃SO₃)₂ can perform one pseudo-catalytic turnover. The volume of benzaldehyde produced by the Cu^{II}(CF₃SO₃)₂ complex alone was taken into account when the turnover numbers for the oxidation reactions were calculated.

Gas chromatographic experiments were performed on an AMS94 apparatus fitted with a Alltach Econo-cap Carbowax column (30 m by 0.25 mm, internal diameter 0.25 μm). The data were obtained using a column and injector temperature of 200 °C, the run time for each experiment was 45 minutes. The data were

processed using the JCL6000 software for Microsoft Windows (version 2.0, revision 26).

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