Syntheses, Structures, and Catalytic Activity of Copper(II)-Aroylhydrazone Complexes

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Abstract. Two Cu^{II} complexes of tridentate Schiff base ligands, $[Cu(L^1)(CH_3OH)_2]NO_3 CH_3OH$ (1) and $[Cu_2(L^2)_2(CH_3OH)_2](NO_3)_2$ (2), were prepared and characterized by elemental analyses and spectroscopic methods $[H_2L^1 = (E)-N$ -(4-hydroxy benzoic acid (2-hydroxy-3-methoxybenzylidene)benzohydrazide, and $H_2L^2 = (E)-N$ -4-hydroxy benzoic acid (5-bromo-2-hydroxybenzylidene)benzohydrazide]. The crystal structures of 1 and 2 were established by X-ray crystallography. The complex cation in 1 is based on a square pyramid with the uninegative Schiff base coordinating in a tridentate mode via O,N,O'-donor atoms with the remaining sites being occupied by two methanol oxygen atoms with one of these in the axial position. By contrast, the

Introduction

Salicylaldehyde benzoylhydrazone (H₂sb) has mild bacteriostatic activity^[1] and inhibits DNA synthesis and cell growth.^[2] The copper(II) complex was shown to be significantly more potent than the metal-free chelate, leading to the suggestion that the metal was the biologically active species. Salicylaldehyde acetylhydrazone (H₂sa) displays radioprotective properties,^[3] and a range of acylhydrazones have been shown to be cytotoxic, the copper complexes again showing enhanced activity. Because of the biological interest in this type of chelate system, several structural studies have been carried out on copper^[4,5] with H₂sb and analogues. Structurally there is a preference for planar, phenolato bridged Cu^{II} dimers with these ligands, which often exhibit antiferromagnetism.^[5,6]

This class of diprotic ligands typically acts as tridentate, planar chelate ligands coordinating through the phenolic and amide oxygen atoms and the imine nitrogen atom. The actual ionization state is dependent upon the reaction conditions and metal employed (Scheme 1). With Cu^{II} in basic media, both

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Schiff base coordinates in a tridentate ligand fashion in dinuclear compound **2** as the phenoxide oxygen atom bridges two central copper atoms. The NO₄ coordination donor set is completed by a methanol oxygen atom, which occupies an axial position in the distorted square pyramidal arrangement. Complexes **1** and **2** are very active catalysts in clean epoxidation reactions using aqueous hydrogen peroxide and acetonitrile. The effects of reaction parameters such as solvent and oxidant in the epoxidation of *cis*-cyclooctene were investigated and showed that cyclooctene and cyclohexene were oxidized efficiently to their corresponding epoxide with 100 and 31% selectivity, respectively, in the presence of catalyst **2**. This catalytic system showed also excellent selectivity in the oxidation of benzyl alcohol.



the phenolic and amide protons are ionized and the ligands coordinate in the enol form.^[7,8] In neutral and mild acidic solution the ligands are monoanionic and coordinate in the keto form. Strongly acidic conditions are necessary to form compounds formulated with a neutral ligand. Catalytic oxidation of hydrocarbons is of great interest to the chemical industry for the conversion petroleum-based feedstocks into useful chemicals such as diols, epoxides, alcohols, and carbonyl compounds.^[9,10] From both economic and environmental perspectives, H_2O_2 and O_2 (or air) are the most attractive oxidants because of their high contents of active oxygen species and co-production of only water. Epoxidation reactions with H₂O₂, one of the "greenest" terminal oxidants, are of great interest due to the importance of epoxides in the manufacture of both bulk and fine chemicals.^[11,12] Epoxidation reactions that use H₂O₂ in conjunction with cheap, manageable and relatively non-toxic metal-based catalysts are potentially viable for largescale production. However, good epoxidation catalysts must activate H₂O₂ without radical formation. Metal-catalyzed epoxidation of alkenes with H2O2 has been reviewed recently.^[13] However, there are a few reports on the copper catalyzed epoxidation of alkenes with H2O2 or other oxidants.[13,14]



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Scheme 1. Keto-enol tautomerization in the ligands.

Herein, we report the synthesis, structures, and catalytic activities of two new copper(II) containing Schiff bases derived from (*E*)-*N*-(4-hydroxy benzoic acid (2-hydroxy-3-methoxybenzylidene)benzohydrazide (H₂L¹) and (*E*)-*N*-4-hydroxy benzoic acid (5-bromo-2-hydroxybenzylidene)benzohydrazide (H₂L²) (Scheme 1). This paper describes their characterization and a description of their catalytic role in the efficient and highly selective epoxidation of alkenes with 30% aqueous H₂O₂.

Results and Discussion

Syntheses of Complexes and Spectroscopy

The Schiff base ligands were synthesized following a literature procedure in one step and in high yield and purity.^[15] The keto-enol tautomerism of the aroylhydrazones H_2L^1 and H_2L^2 is illustrated in Scheme 1. IR spectroscopy confirmed that in the solid state each of these ligands exists as the keto tautomer. Copper complexes with hydrazone Schiff base ligands were prepared by treating a methanol solution of the respective ligand with an equimolar amount of $Cu(NO_3)_2$ ·3H₂O (Scheme 2).



Scheme 2. Syntheses of complexes 1 and 2.

The molar conductance (Λ_M) for $[Cu(HL^1)(CH_3OH)_2]NO_3$ · CH₃OH (1) in methanol solution was 79 ohm⁻¹·cm²·mol⁻¹, a value consistent with a 1:1 electrolyte type (80–115 ohm⁻¹· cm²·mol⁻¹).^[16] For $[Cu_2(HL^2)_2(CH_3OH)_2](NO_3)_2$ (2), the molar conductance of 129 ohm⁻¹·cm²·mol⁻¹ was observed, which is slightly lower than that expected for 2:1 electrolytes (160– 220 ohm⁻¹·cm²·mol⁻¹). This difference can be related to the high molecular weight of dinuclear **2**, which decreases mobility in solution.

A list of salient IR spectroscopic data is presented in Table 1. A comparison of the spectra of the complexes with the ligands provides evidence for the coordination mode of the ligands in the complexes. For example, the presence of a N-H band, and shifts in the azomethine (-C=N-, 4 cm⁻¹) and carbonyl bands (6 cm⁻¹) of (HL¹)⁻ compared to free ligand H_2L^1 indicate coordination of $(HL^1)^-$ through the phenolate oxygen, azomethine nitrogen, and amide oxygen atoms in complex 1. Appearance of the carbonyl stretching vibration band, v(C=O), with slight shift supports the presence of the coordinated $(HL^1)^-$ and $(HL^2)^-$ in keto form in 1 and 2, respectively. This finding also suggests that the -N-C=O bond is delocalized to a certain extent in the free and the coordinated ligands. Presence of the delocalization was supported by observation that vibrational stretching of the ligand C-O is among the lowest v(C=O) of the reported aroylhydrazone ligands [v(C=O) 1649–1673 cm⁻¹].^[15] That **1** and **2** are ionic complexes is demonstrated by the presence of the nitrate counterion as indicated by the intense absorption at 1383 and 1372 cm⁻¹, respectively.

Table 1. Selected IR spectroscopic data of the ligands and complexes $/cm^{-1}$.

Compound	v(O–H)	v(N–H)	v(C=O)	v(C=N)
H_2L^1	3451 (m)	3215 (w)	1646 (w)	1610 (s)
H_2L^2	3433 (m)	3219 (m)	1624 (s)	1606 (s)
1	3408 (w)	3283 (m)	1652 (w)	1606 (s)
2	3419 (m)	3171 (m)	1631 (m)	1612 (s)

As a result of complexation, the UV/Vis spectra in methanol show absorbance bands at λ_{max} (ϵ , dm³·mol⁻¹·cm⁻¹) = 239 (45,500), 322 (37,000), 391 (20,000), and 685 nm (46) for complex 1, and at λ_{max} (ϵ , dm³·mol⁻¹·cm⁻¹) = 230 (78,000), 310 (84,000), 403 (45,000), and 670 nm (79) for complex 2 (Figure 1). The complexes show UV/Vis spectra similar to their corresponding ligands. Based on their extinction coefficients they can be assigned to intraligand $\pi \rightarrow \pi^*$ (230, 239 nm) and $n \rightarrow \pi^*$ (310, 322 nm) transitions. The higher energy bands at 391 nm (complex 1) and 403 nm (complex 2) with high extinction coefficient values are due to the coordinated phenolate oxygen atom to Cu^{II} charge transfer (LMCT) transitions. Furthermore, the complexes 1 and 2 show ligand field d-dtransitions at 685 (46) and 670 nm (79), respectively (the insets in Figure 1a and b). The later finding suggests very similar coordination environments for the central Cu^{II} atoms.

Crystallography

Unambiguous structure determination for 1 and 2 was achieved by X-ray crystallography. The crystallographic asymmetric unit of 1 comprises a complex cation, a nitrate anion, and a solvent methanol molecule (Figure 2). As indicated by spectroscopy, the Schiff base is uninegative and coordinates in



Figure 1. UV/Vis spectra recorded in methanol of (a) **1** and H_2L^1 (*c* = 2×10^{-5} M), and (b) **2** and H_2L^2 (*c* = 1.165×10^{-5} M). The insets show d-d transitions in the Cu^{II} (*c* = 1×10^{-3} M).

a tridentate mode via the O,N,O'-donor atoms. The remaining sites in the pentacoordinate arrangement are occupied by two methanol oxygen atoms. The coordination sphere is best described as distorted square pyramidal in accordance with the value of the trigonality index $[\tau = (\beta - a)/60^\circ = 0.11]$, where a and β are the largest angles in the coordination sphere.^[17] In this description, the methanol-O5 atom occupies an axial position. The long distance of the Cu1-O5 bond with 2.2552(18) Å shows weak bonding of the methanol to the central copper atom due to the Jahn-Teller effect.^[18] The bond lengths in 1 and 2 (see captions to Figure 2 and Figure 3 for selected geometric parameters) are within the expected range for copper(II) complexes with Schiff base ligands.^[19] The entire Schiff base ligand HL¹ is close to being planar with a small twist exhibited by the hydroxybenzene group from the remaining atoms; the dihedral angle between the two benzene rings is 3.54(12)°. This overall planarity is consistent with the observation that each of the five- and six-membered chelate rings is planar having r.m.s. deviations of 0.040 and 0.011 Å, respectively.

A different mode of coordination of the Schiff base ligand is observed in 2. The key difference is the dimerization of the molecule about a center of inversion as the phenoxide-O1 atom



Figure 2. Molecular structures of the complex cation, nitrate anion and solvent methanol molecule in **1**. Key geometric parameters: Cu–O2 1.8982(16), Cu–O3 1.9905(16), Cu–O5 2.2552(18), Cu–O6 1.9610(17), Cu–N1 1.9201(19), O3–C9 1.257(3), C9–N2 1.353(4) Å; O2–Cu–O3 172.39(7), O6–Cu–N1 165.91(8)°.



Figure 3. The molecular structure of the dinuclear cation in **2**; the nitrate anions are omitted for clarity. Unlabelled atoms are related across a center of inversion (*i*: 1–*x*, 1–*y*, 1–*z*). Key geometric parameters: Cu–O1 1.9406(15), Cu–O2 1.9493(15), Cu–O4 2.2396(16), Cu–O1^{*i*} 1.9853(15), Cu–N1 1.9406(18), O2–C8 1.263(3), C8–N2 1.348(3) Å; O1–Cu–O2 169.48(7), O1^{*i*}–Cu–N1 163.71(7)°.

bridges asymmetrically two central copper atoms [Cu–O1 1.985(2) Å / Cuⁱ–O1 1.941(2) Å] with the concomitant exclusion of one of the coordinating methanol molecules seen in **1**; the remaining methanol oxygen atom occupies the axial position in **2** (Figure 3). The NO₄ coordination donor set defines a distorted square-pyramidal coordination arrangement ($\tau = 0.10$). The five- and six-membered chelate rings are planar (r.m.s. deviations = 0.027 and 0.057 Å, respectively) but a slightly greater twist in the overall Schiff base molecule [dihedral angle between the benzene rings = 12.96(10)°] is observed in **2** compared with the situation in **1**.

The hydrazone ligands HL^1 and HL^2 are monoanionic and coordinate in the keto form, which can be verified from C–O and C–NH bond lengths of the amide unit: O3–C9 1.257(3) Å, C9–N2 1.353(4) Å in **1** and O2–C8 1.263(3) Å, C8–N2 1.348(3) Å in **2** (see Figure 2 and Figure 3). Amide unit bond lengths for aroyl hydrazones are in the ranges of 1.218–1.292 Å (C–O), 1.313–1.365 Å (C–N), and 1.284–1.314 Å (C–O), 1.291–1.331 Å (C–N) in the keto and enol form, respectively.^[20]

As anticipated from the chemical composition, significant hydrogen bonding interactions are present in the crystal structures of **1** and **2**. In **1**, the solvent methanol molecule straddles

three hydrogen bonding sites in the oxygen-rich bay of the complex cation (Figure 4a), and the resulting two molecule aggregates are connected into a linear supramolecular chain along the *b* axis by hydrogen bonds formed between nitrate oxygen atoms and the hydroxyl hydrogen and hydrazide hydrogen bond with the axially coordinated methanol of an inversion related molecule so that a double layer parallel to (101) ensures (Figure 4b). The most prominent interactions between layers are of the type π ···· π , where the π systems are the five-and six-membered chelate rings; such interactions are increasingly being recognized as supramolecular synthons.^[21] While the π ··· π interactions bring copper atoms into close proximity, the Cu···Cu separation of 3.9235(6) Å is not considered to represent significant bonding interactions between these atoms.



Figure 4. Crystal packing in 1: (a) supramolecular chain sustained by O–H···O and N–H···O hydrogen bonds shown as dashed lines; (b) double layers sustained by O–H···O hydrogen bonds are formed in the (101) plane. Connections between the layers are mediated by π (Cu-OCN₂)··· π (CuO₂C₃N) interactions (dashed lines).

The crystal packing in **2** bears some similarities to that found in **1**. Supramolecular chains along [1 -1 1] are formed by hydrogen bonds formed between nitrate oxygen atoms with the hydroxyl hydrogen and hydrazide hydrogen atoms.^[22] Owing to symmetry, these are formed on both sides of the dinuclear molecule and result in the formation of centrosymmetric 24-membered {…ONO…HNC₅OH}₂ synthons (Figure 5a). Inversion related chains are connected by bifurcated methanol-OH…O-nitrate hydrogen bonds into layer parallel to (011) (Figure 5b). The most prominent interactions between the layers are of the type methyl-C–H…O-nitrate.^[23]



Figure 5. Crystal packing in 2: (a) supramolecular chain sustained by $O-H\cdots O$ and $N-H\cdots O$ hydrogen bonds shown as dashed lines; (b) view of the unit cell contents in projection down the *a* axis highlighting the stacking of layers and the C-H···O connections between them (dashed lines).

Catalytic Activities

The catalytic activities of the complexes were first tested in the oxidation of *cis*-cyclooctene. In this regard, we were particularly interested to evaluate the advantages of H_2O_2 as a green and inexpensive terminal oxidant. The catalyzed oxidation of *cis*-cyclooctene was carried out with H_2O_2 to give *cis*-cyclooctene oxide as the sole product. Control experiments revealed that the presence of oxidant and catalyst were essential for the oxidation. While H_2O_2 is a widely used oxidant with high active oxygen content^[24] it is rather slow in the absence of activators. Oxidation of *cis*-cycloocetene was achieved only up to 11% conversion under optimal conditions by Cu(NO₃)₂·3H₂O (0.0011 mmol)/H₂O₂ (3 mmol) at 80 °C after 5 h.

The catalytic activities of complexes 1 and 2 show a similar trend in the oxidation of *cis*-cycooctene with slight higher activity for 2, as shown in Figure 6. This finding reflects their structural similarity and the presence of similar coordination environments for Cu^{II} in each complex.

To determine the optimal experimental conditions, the effects of H_2O_2/cis -cyclooctene molar ratio, reaction temperature, and influence of solvent were studied. We have monitored the progress of *cis*-cyclooctene epoxidation for different molar ratios of oxidant and substrate (Figure 7). Molar H_2O_2/cis -cyclooctene ratios of 1, 2 and 3 were considered, while keeping a fixed amount of *cis*-cyclooctene (1.0 mmol) and catalyst (1.0 mg) in 3 mL of acetonitrile at 80 °C. At a ratio of oxidant: alkene of 1:1, conversion occurred up to 42% after 5 h. Increasing the H_2O_2/cis -cyclooctene ratio to 2:1 increased the conversion from 42 to 54% after 5 h. Further increase in the ratio to 3:1 gave additional increase of the conversion, 64% after 5 h. Hence, a H_2O_2/cis -cyclooctene ratio of 3:1 was selected for further studies. Oxidant requirements of the order



Figure 6. Effects of the catalyst on the oxidation of cyclooctene. Reaction conditions: catalyst 1.0 mg, CH₃CN 3.0 mL, cyclooctene 1.0 mmol, chlorobenzene 0.1 g, H₂O₂ 1.0 mmol and temperature 60 ± 1 °C. [H₂O₂]/[cyclooctene] ratio 1:1.



Figure 7. Effect of H_2O_2 concentration on the oxidation of cyclooctene by **2.** Reaction conditions: catalyst $[Cu_2(HL^2)_2(CH_3OH)_2](NO_3)_2$ (**2**) 1.0 mg (0.0011 mmol), CH₃CN 3.0 mL, cyclooctene 1.0 mmol, chlorobenzene 0.1 g, temperature 60 ± 1 °C.

of 10:1 epoxidation reactions have been documented in the literature. $\ensuremath{^{[25,26]}}$

The oxidation of cyclooctene was studied at 20, 40, 60, and 80 °C. Increasing the reaction temperature resulted in significantly higher yields of *cis*-cyclooctene oxide (Figure 8). A yield of 73 % was achieved at 80 °C after 5 h.

The catalytic efficiency was studied in a variety of solvents (Figure 9). Catalytic activity of **2** was lowest in chloroform with conversion of 25 % after 5 h. Oxidation of *cis*-cyclooctene increased when ethanol (conversion 54 %) and methanol (conversion 61 %) were used as solvents. The best performance of the catalyst was observed in acetonitrile (conversion 73 % after 5 h), possibly due to its dielectric constant ($\varepsilon/\varepsilon_0 = 37.5$), which is the highest of all the solvents used. It is the optimal polarity of acetonitrile, which enables dissolution of both alkene and H₂O₂. That is likely to be factor facilitating the epoxidation reaction. Furthermore, the improvement in the *cis*-cyclooctene



Figure 8. Effect of the reaction temperature on the oxidation of cyclooctene by **2**. Reaction conditions: catalyst **2** 1.0 mg (0.0011 mmol), CH₃CN 3.0 mL, cyclooctene 1.0 mmol, chlorobenzene 0.1 g, H_2O_2 3.0 mmol.



Figure 9. Effect of solvent on the oxidation of cyclooctene by 2. Catalyst 1.0 mg (0.0011 mmol), cyclooctene 1.0 mmol, solvent 3.0 mL, chlorobenzene 0.1 g, aqueous 30% H₂O₂ 3.0 mmol, temperature 80 ± 1 °C.

conversion with change of solvent from methanol ($\varepsilon/\varepsilon_0 = 32.7$) to acetonitrile suggests the possible involvement of acetonitrile in the oxidation of cyclooctene by H₂O₂. This idea was not supported by the absence of acetamide in the GC analyses and in the ¹H NMR spectra of *cis*-cyclooctene oxidation products. Bases such as NaOH and KOH are known to catalyze the epoxidation of alkenes by using H₂O₂ in the presence of nitriles.^[27] The catalyst decomposes H₂O₂ to some extent but the decomposition rate is much lower than H₂O₂ activation for oxidation of hydrocarbons.

With the optimal reaction conditions for this catalyst to hand, we proceeded to investigate the scope for other hydrocarbons. The molar ratio of catalyst:H₂O₂:hydrocarbon for these experiments was 1:3000:1000. The results for the catalytic oxidation of different substrates are summarized in Table 2. *Cis*-cyclooctene, cyclohexene and benzyl alcohol were oxidized. Cyclohexene gave the corresponding epoxide as the main product with 48 % selectivity, other products were 2-cyclohex-1-ol (selectivity 35 %) 2-cyclohex-1-one (selectiv-

Substrate	Product(s)	Selectivity ^{b)} /%	Conversion ^{c)} /%	TON ^{d)}	TOF ^{e)} /h ⁻¹
Cyclooctene	Epoxide	100	73	365	73
Cyclohexene	Epoxide ^{f)}	48	65	325	65
	Enol ^{g)}	35			
	Enone ^{h)}	17			
Benzyl alcohol	Aldehyde	100	43	215	43

Table 2. Oxidation of various substrates catalyzed by 2^{a} .

a) Reaction conditions: Catalyst $[Cu_2(HL^2)_2(CH_3OH)_2](NO_3)_2$ (2) 1.0 mg (1.0 µmol), CH₃CN 3.0 mL, substrate 1.0 mmol, H₂O₂ 3.0 mmol, chlorobenzene 0.1 g, time 5 h, temperature 80 ± 1 °C. b) Selectivity = ([desired product]/[conversion]) × 100. c) Conversions are based on the starting substrate and determined by GC analysis. d) TON: turnover number = number of moles of product formed per mole of copper in the catalyst. e) TOF: turnover frequency = number of moles of product formed per mole of copper in the catalyst per unit time = (Conv. × 1.0 mmol)/ (0.001 mmol × 5 h). f) Cyclohexene oxide. g) 2-Cyclohexene-1-ol. h) 2-Cyclohexene-1-one.

ity 17%). Cyclohexene is more prone to both epoxidation and allylic oxidation^[28] and oxygenation of cyclohexene is a good probe to provide evidence for or against a non-radical mechanism and to evaluate the catalyst selectivity. We observed for cyclooctene and cyclohexene oxidation a decrease in product yields when O₂ was absent (conversions 55% for cyclohexene and 65% for cyclooctene) by repeating the reaction in a nitrogen atmosphere. This finding confirms the presence of free diffusing radicals as intermediate. Free diffusing radicals are greatly enhanced because of radical chains in the presence of O₂.

Conclusions

This work revealed that coordination complexes of Cu^{II} with polydentate hydrazone Schiff base ligands obtained by reaction of 2-hydroxybenzhydrazide and 2-hydroxy-3-methoxybenzaldehyde derivatives afford a new class of Cu^{II} catalysts for the oxidation of alkenes and benzylalcohol. It was demonstrated that these dissymmetric hydrazone copper(II) complexes are highly selective catalysts for the oxidation of cyclooctene, cyclohexene, and benzyl alcohol by H_2O_2 under mild conditions.

Experimental Section

All solvents and materials were purchased in high purity from Merck and Fluka. IR spectra were taken with a Matson FT-IR spectrophotomer in the range of 400–4000 cm⁻¹ as KBr disks. UV/Vis spectra of solutions were recorded with a Shimadzu 160 spectrophotometer. A HP Aglient 6890 gas chromatograph, which was equipped by HP-5 capillary column (phenyl methyl siloxane 30 mm × 320 μ m × 0.25 μ m), a flame-ionization detector and gas chromatograph-mass spectrometer (Hewlett-Packard 5973 Series MS-HP gas chromatograph with a mass-selective detector) was used for identification of the oxidation reaction products. The Schiff base ligands H₂L¹ and H₂L² were prepared according to a reported procedure.^[15]

Synthesis of $[Cu(HL^1)(CH_3OH)_2]NO_3 \cdot CH_3OH$ (1): Single crystals of $[Cu(HL^1)(CH_3OH)_2]NO_3 \cdot CH_3OH$ (1) were obtained by the thermal gradient method. Molecule H_2L^1 (0.02 g, 0.07 mmol) and $Cu(NO_3)_2 \cdot$ $3H_2O$ (0.03 g, 0.12 mmol) were placed in the main arm of a branched tube. Methanol (10 mL) was carefully added to fill the arms, the tube was sealed and the arm containing reagents was immersed in an oil bath at 60 °C, while the other arm was kept at ambient temperature. After 10 d, blue crystals of **1** were deposited in the cooler arm, which were filtered off, washed with methanol and dried in air. Yield: 95 % (51.7 mg). M.p.: 273 °C. $C_{18}H_{25}CuN_3O_{10}$ (506.95): calcd. C 42.65, H 4.97, N 8.29, Cu 12.53 %; found C 42.61, H 4.99, N 8.26, Cu 12.63 %. **IR** (KBr): $\tilde{\nu}$ = 3408 (w, O–H), 3283 (m, N–H), 1606 (s C=O), 1568 (s, C=N), 1383 (vs, NO_3^-) cm^{-1}. **UV/Vis** (methanol): λ_{max} (ϵ , dm³ mol⁻¹ cm⁻¹) = 239 (45,500), 322 (37,000), 391 (20,000) and 685 nm (46).

Synthesis of [Cu₂(HL²)₂(CH₃OH)₂](NO₃)₂ (2): Complex [Cu₂(HL²)₂-(CH₃OH)₂](NO₃)₂ (2) was synthesized and olive-green single crystals grown by a procedure similar to the synthesis of complex 1 but using H₂L². Yield: 90% (51.2 mg). M.p.: 282 °C. C₃₀H₂₈Br₂Cu₂N₆O₁₄ (983.48): calcd. C 36.64, H 2.87, N 8.55, Cu 12.92%; found C 36.65, H 2.89, N 8.44, Cu 13.03%. IR (KBr): $\tilde{v} = 3419$ (m, O–H), 3171 (m, N–H), 1631 (m, C=O), 1612 (s, C=N), 1372 (vs, NO₃⁻) cm⁻¹. **UV/Vis** (methanol): λ_{max} (ε, dm³ mol⁻¹ cm⁻¹) = 230 (78,000), 310 (84,000), 403 (45,000) and 670 nm (79).

X-ray Crystallography: Intensity data for 1 and 2 were measured at 100 K with an Agilent Technologies SuperNova Dual CCD with an Atlas detector fitted with Cu- K_{α} radiation so that $\theta_{\text{max}} = 76.6^{\circ}$ (1) and 76.3° (2). Data processing and absorption correction were accomplished with CrysAlis PRO.^[29] The structures were solved by direct methods with SHELXS-97^[30] and refinement (anisotropic displacement parameters, C-bound hydrogen atoms in the riding model approximation and a weighting Scheme of the form $w = 1/[\sigma^2(F_0^2) +$ $(aP)^2 + bP$ for $P = (F_0^2 + 2F_c^2)/3$) was on F^2 by means of SHELXL-97.^[30] For 1, the O- and N-bound hydrogen atoms were located from a difference map and refined with distance restraints of 0.84 and 0.88 Å, respectively. For 2, the O- and N-bound hydrogen atoms were again located from a difference map and refined with 0.84 ± 0.01 and 0.88 ± 0.01 Å, respectively. Crystallographic data and final refinement details are given in Table 3. Figure 2 and Figure 3 were drawn with ORTEP-3 for Windows^[31] at the 70% probability level and the remaining crystallographic figures were drawn with DIAMOND using arbitrary spheres.^[32]

General Oxidation Procedure: The liquid phase catalytic oxidations were carried out in air (atmospheric pressure) in a 25 mL round-bottomed flask equipped with a magnetic stirrer and immersed in a thermostatted oil bath at 80 or 60 °C. In a typical experiment, a mixture of $30 \% H_2O_2$ (3 mmol), solvent (3 mL), chlorobenzene (0.1 g) as internal standard, and cyclooctene (1 mmol) was added to a flask containing the catalyst, i.e. 1 or 2. The course of the reaction was monitored using a gas chromatograph equipped with a capillary column and a flame ionization detector. The oxidation products were identified by comparing their retention times with those of authentic samples or alternatively by ¹H NMR and GC-mass analyses. Yields based on the added substrate were determined by a calibration curve. Control reactions were carried out in the absence of catalyst and H_2O_2 under the same

Table 3. Crystal data and refinement details for 1 and 2.

	1	2	
Formula	C ₁₈ H ₂₅ CuN ₃ O ₁₀	C ₃₀ H ₂₈ Br ₂ Cu ₂ N ₆ O ₁₄	
Formula weight	506.95	983.48	
Crystal color	blue	olive-green	
Crystal dimensions /mm	$0.10 \times 0.20 \times 0.30$	$0.15 \times 0.25 \times 0.35$	
Crystal system	triclinic	triclinic	
Space group	ΡĪ	$P\bar{1}$	
a/Å	9.7384(8)	7.4497(3)	
b /Å	11.1472(9)	10.4994(5)	
c /Å	11.2985(10)	11.5358(5)	
a /°	60.855(9)	99.599(4)	
β /°	88.886(7)	95.081(4)	
γ /°	79.792(7)	104.917(4)	
V/Å ³	1051.08(15)	851.46(6)	
Z	2	1	
$D_{\rm x}$ /g·cm ⁻³	1.602	1.918	
F(000)	526	490	
$\mu(Cu-K_a)/mm^{-1}$	2.029	4.997	
Reflections collected	7835	6161	
R _{int}	0.027	0.020	
Unique reflections	4303	3478	
Obs. reflections $[I >$	3921	3393	
2σ(<i>I</i>)]			
R [obs. reflns]	0.044	0.029	
a, b, in weighting	0.080, 1.084	0.054, 0.753	
scheme			
wR (all data)	0.128	0.083	

conditions. These runs confirmed that no products, or at most, only trace yields, were detected.

Some degradation of the ligand was obvious from changes in solution color from light green to pale yellow after 5 h.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-894934 (1) and CCDC-894935 (2) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac. uk)

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