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Copper(II) complexes of pyridine-oxazoline (Pyox) ligands: Coordination chemistry, ligand stability, and catalysis

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ABSTRACT

The coordination chemistry of copper(II) complexes bearing pyridine-oxazoline ("Pyox") ligands has been studied, with an aim of investigating their catalytic ability. Interestingly, the stability of the coordinated ligands has been shown to be much less than previously assumed: hydrolysis of the ligands by fortuitous water gives rise to 2-pyridine carboxylate formation, which encapsulate the copper in a two-dimensional coordination polymer **3**. The complexes [Cu(R-Pyox)(NCMe)$_2$(ClO$_4$)$_2$] {R = benzyl (Bn) **2a**, phenyl (Ph) **2b**, isopropyl (^{i}Pr) **2c**} have been prepared, of which the benzyl derivative has been analysed by CW EPR spectroscopy. The complex [Cu(Bn-Pyox)(NCMe)$_2$(ClO$_4$)$_2$] and the afore-mentioned coordination polymer have been crystallographically characterised. The performance of complexes **2a–c** in the asymmetric allylic oxidation of cyclohexene is described.

1. Introduction

The continued development of metal catalysts is supported by studies into the coordination chemistry of complexes bearing supporting ligands commonly employed in catalysis. These studies are particularly important when complex ligands are employed, that may themselves become the focus of chemical transformations in direct competition with the catalytic substrates. Ligand-based (undesired) chemical transformations are numerous; common examples include C—H activation of side-chains [1], the epimerisation of chiral ligands, [2a] the ring-opening of cyclic ligand architectures [2a] and the reaction of coordinated imine ligands [2b] in the presence of Lewis acidic transition metals. A detailed understanding of these processes is crucial if catalyst performance is to be rationalised so that catalyst optimisation can be attained.

It is in this context that we sought to elucidate the coordination chemistry of copper supported by pyridine-oxazoline "Pyox" ligands. Pyox ligands have been successfully employed as chiral supporting ligands for a range of catalytically active complexes, *e.g.* in the rhodium-catalysed asymmetric hydrosilylation of carbonyl compounds [3]. However, their wider application has been somewhat less forthcoming; for example their complexes with copper(I) have been studied in the asymmetric Kharasch–Sosnovsky reaction, but the enantiomeric excesses were significantly lower than similar ligand systems [4]. In the afore-mentioned Kharasch–Sosnovsky reaction, the copper(I) complexes were prepared *in situ*, and therefore there are a number of unanswered questions pertaining to the coordination environment involving the Pyox ligand, that may offer some explanation as to the observed activity and selectivity in such catalytic transformations. Consequently, we set out to prepare and characterise copper complexes with Pyox ligands in order that the stability of such complexes could be adequately assessed.

Whilst Pyox ligands have been used in copper-catalysis, such as cyclopropanation [5] and allylic oxidation [4], their structural coordination chemistry is much more limited. A search of the Cambridge Structural Database provides five examples of structurally characterised copper complexes bearing Pyox derivatives, of which three feature the five-coordinate copper centre coordinated by two Pyox ligand fragments along with a halide coligand [6–8]. The only crystallographically characterised copper–Pyox complexes, in which only one Pyox moiety is coordinated to the copper, have been reported by Brunner [9] and Breit [10]. Once again, both complexes are five-coordinate, as is common for copper(II), and both also contain halide co-ligands. Most noticeable is the total absence of copper–Pyox complexes that do not contain halides; this is an important omission, since the most common counterions employed in catalysis are those that are unrepresented in these studies, such as PF_6^- and $CF_3SO_3^-$.

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2. Experimental

2.1. General information

All air sensitive preparations were carried out under an atmosphere of argon or of dinitrogen using standard glove box or Schlenk techniques. Solvents were purified by distillation from calcium hydride (chloroform), or by passing through a column of activated alumina using an MBraun SPS-800 solvent purification system (ethanol, acetonitrile).

Samples for NMR spectroscopy were prepared in 5 mm Wilmad NMR tubes and spectra were measured on Bruker DPX-250 and Avance 400 NMR spectrometers. Spectra were referenced internally to residual protio solvent resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Mass spectra were measured on a Waters LCT Premier XE by the mass spectrometry service at the Cardiff University School of Chemistry. Elemental analyses were measured by the analytical services at London Metropolitan University.

The CW-EPR measurements were recorded on an X-band Bruker EMX spectrometer operating at 100 kHz field modulation, 10 mW microwave power and equipped with a high sensitivity cavity (Bruker ER 4119HS). EPR computer simulations were performed using the SimEPR32 program [11], and g values were determined using a DPPH standard. For EPR measurements, 0.5 ml of a 3×10^{-2} M solution of **2a** in MeCN was diluted with toluene (0.5 ml) and a drop of DMF added. 200 μl of the solution was placed into an EPR tube (4 mm Suprasil) under argon, and the sample frozen immediately for the analysis. UV–Vis. studies were performed on a Jasco V-570 spectrometer as 2 mmol dm^{-3} solutions.

2.2. Synthesis of ligands

Amino alcohols were prepared by the reduction of the corresponding amino acid. All other reagents were obtained from commercial suppliers and used as received unless stated.

2.2.1. 2-Pyridinecarboxyimidate

Sodium metal (0.044 g, 1.91 mmol) was added to a solution of 2-cyanopyridine (2 g, 19.21 mmol) in EtOH (30 ml) and stirred at room temperature for 24 h. Glacial acetic acid (0.12 ml, 2.09 mmol) was then added to quench the reaction and the solvent removed under reduced pressure. The crude product was dissolved in CH_2Cl_2 (50 ml), washed with water (2×50 ml), brine (10% w/v, 50 ml) and dried over Na_2SO_4. After filtering, the solvent was removed under reduced pressure to give the product as a light brown oil. Yield = 2.71 g (94%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 293 K) $\delta = 9.03$ (1H, br s, N*H*), 8.53 (1H, d, $^3J_{HH} = 5.6$ Hz, py*H*), 7.78 (1H, d, $^3J_{HH} = 7.9$ Hz, py*H*), 7.70 (1H, dd, $^3J_{HH} = 7.7$ and 5.6 Hz, py*H*), 7.27 (1H, m, py*H*), 4.36 (2H, q, $^3J_{HH} = 7.1$ Hz, CH_2), 1.37 (3H, t, $^3J_{HH} = 7.1$ Hz, CH_3) ppm.

The ligand precursors R-Pyox {R = benzyl (Bn, **1a**), phenyl (Ph, **1b**), isopropyl (^{i}Pr, **1c**)} were prepared using a modified literature procedure and data were consistent with reported values [3,12]. Spectroscopic data are reported here for convenience and completeness.

2.2.2. Bn-Pyox (*1a*)

2-Pyridinecarboxyimidate (0.523 g, 3.48 mmol) and L-phenylalaninol (0.527 g, 3.48 mmol) in $CHCl_3$ (15 ml) were heated at 60 °C for 16 h. The organic solution was washed with water (2×30 ml), brine (10% w/v, 30 ml) and dried over Na_2SO_4. After filtering, the solvent was removed under reduced pressure to give the product as an off-white solid. Yield = 0.739 g (89%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 293 K) $\delta = 8.62$ (1H, d, $^3J_{HH} = 5.9$ Hz, py*H*), 7.97 (1H, d, $^3J_{HH} = 7.9$ Hz, py*H*), 7.60 (1H, dd, $^3J_{HH} = 7.9$ and 5.9 Hz, py*H*), 7.30 (1H, m, py*H*), 7.26–7.06 (5H, m, Ph*H*), 4.58 (1H, m, C*H*Bn), 4.36 (1H, app. t, app. $J_{HH} = 9.0$ Hz, C*H*HO), 4.13 (1H, app. t, app. $J_{HH} = 8.1$ Hz, CH*H*O), 3.32 (1H, dd, $^2J_{HH} = 13.2$ Hz, $^3J_{HH} = 5.1$ Hz, CH*H*Ph), 2.56 (1H, dd, $^2J_{HH} = 13.0$ Hz, $^3J_{HH} = 5.2$ Hz, C*H*HPh) ppm. ES-MS: m/z (%) = 239.13 (100) [Bn-Pyox+H]$^+$.

2.2.3. Ph-Pyox (*1b*)

Prepared similarly from 2-pyridinecarboxyimidate (0.508 g, 3.38 mmol) and D-phenylglycinol (0.464 g, 3.38 mmol). Yield = 0.728 (96%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 293 K) $\delta = 8.67$ (1H, d, $^3J_{HH} = 6.0$ Hz, py*H*), 8.08 (1H, d, $^3J_{HH} = 7.9$ Hz, py*H*), 7.71 (1H, app. t, $^3J_{HH} = 7.9$ Hz, py*H*), 7.36 (1H, m, py*H*), 7.30–7.18 (5H, m, Ph*H*), 5.38 (1H, app. t, app. $^3J_{HH} = 8.6$ Hz, C*H*Ph), 4.81 (1H, app. t, app. $J_{HH} = 8.6$ Hz, C*H*HO), 4.30 (1H, app. t, app. $J_{HH} = 8.5$ Hz, CH*H*O) ppm. ES-MS: m/z (%) = 225.10 (100) [Ph-Pyox+H]$^+$.

2.2.4. ^{i}Pr-Pyox (*1c*)

Prepared similarly from 2-pyridinecarboxyimidate (0.524 g, 3.49 mmol) and L-valinol (0.360 g, 3.49 mmol). Yield = 0.604 g (91%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 293 K) $\delta = 8.65$ (1H, d, $^3J_{HH} = 5.8$ Hz, py*H*), 8.03 (1H, d, $^3J_{HH} = 7.9$ Hz, py*H*), 7.72 (1H, app. t, $^3J_{HH} = 7.8$ Hz, py*H*), 7.33 (1H, m, py*H*), 4.46 (1H, app. t, $^3J_{HH} = 8.0$ Hz, C*H*^{i}Pr), 4.18–4.04 (2H, m, CH_2O), 1.85 {1H, sept, $^3J_{HH} = 6.8$ Hz, C*H*(CH_3)$_2$}, 1.00 {3H, d, $^3J_{HH} = 6.8$ Hz, CH(CH_3)(CH_3)}, 0.89 (3H, d, $^3J_{HH} = 6.8$ Hz, CH(CH_3)(CH_3)} ppm. ES-MS: m/z (%) = 191.12 (100) [^{i}Pr-Pyox+H]$^+$.

2.3. Synthesis of complexes

2.3.1. General procedure for the preparation of *[Cu(R-Pyox)(NCMe)$_2$(ClO$_4$)$_2$]* (*2*)

To a solution of $[Cu(H_2O)_6][ClO_4]_2$ (74.1 mg, 0.200 mmol) [*warning: perchlorates can be dangerous – this procedure should not be scaled up without appropriate precautions*] in acetonitrile (3.0 ml) was added a solution of R-Pyox (0.200 mmol) in acetonitrile (3.0 ml). The resulting blue/green solution was allowed to stir for 12 h under argon before removing the volatiles under reduced pressure (Schlenk line vacuum). The solid residue was washed with diethyl ether (2×5 ml), extracted into acetonitrile (10 ml), filtered through Celite to remove any insoluble residues, and the solvent removed from the filtrate under reduced pressure. The solid product was dried *in vacuo* for 3 h at room temperature to 1.0×10^{-2} mbar to afford the complex as a blue/green powder. Elemental combustion analyses were consistent with the title complexes without the coordinated acetonitrile.

2.3.2. *[Cu(Bn-Pyox)(NCMe)$_2$(ClO$_4$)$_2$]* (*2a*)

IR data (KBr pellet, cm^{-1}): 3411 (br), 3323 (m), 3247 (m), 3194 (m), 3065 (m), 3025 (m), 2963 (m), 2921 (m), 2854 (m), 2015 (w), 1891 (w), 1653 (s), 1595 (s) 1570 (m), 1497 (s), 1453 (m), 1414 (s) 1300 (m), 1261 (s), 1142 (s), 1110 (s), 1086 (s), 1023 (s), 926 (m), 799 (s), 747 (m), 703 (m), 675 (m), 623 (s), 515 (w), 492 (w), 464 (w). ES-MS: m/z (%) = 399.99 [Cu(Bn-Pyox)(ClO$_4$)]$^+$ (100), 441.02 [Cu(Bn-Pyox)(MeCN)(ClO$_4$)]$^+$ (97), 423.06 [Cu(Bn-Pyox)(2-Py-CO$_2$)]$^+$ (24), 269.57 [Cu(Bn-Pyox)$_2$]$^{2+}$ (16); HR ES-MS for [Cu(Bn-Pyox)(MeCN)(ClO$_4$)]$^+$: m/z = 441.0144 (calc. for $C_{17}H_{17}ClCuN_3O_5$: 441.0153). UV–Vis (MeCN): λ_{max} (ε dm^3 mol^{-1} cm^{-1}) = 694 nm (40.9). *Anal.* Calc. for $C_{15}H_{14}Cl_2CuN_2O_9$: C, 35.98; H, 2.82; N, 5.59. Found: C, 35.91; H, 2.99; N, 5.88%.

2.3.3. *[Cu(Ph-Pyox)(NCMe)$_2$(ClO$_4$)$_2$]* (*2b*)

IR data (KBr pellet, cm^{-1}): 3407 (br), 3326 (m), 3260 (m) 3195 (m), 3070 (m), 2929 (m), 2250 (w), 2019 (w), 1893 (m), 1828 (w), 1652 (s), 1591 (s), 1571 (m), 1496 (m), 1456 (m), 1405 (s), 1330 (w), 1300 (m), 1265 (m), 1149 (s), 1109 (s), 1084 (s), 1028 (m),

Table 1
X-ray experimental data of **2a** and **3**.

	2a	**3**
Empirical formula	$C_{38}H_{40}Cl_4Cu_2N_8O_{18}$	$C_{18}H_{14}ClCu_2N_3O_{11}$
Formula weight	1165.68	610.85
Crystal size (mm)	0.20 × 0.15 × 0.15	0.10 × 0.03 × 0.03
λ (Å)	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.828(2)	8.562(2)
b (Å)	10.076(2)	10.268(2)
c (Å)	14.925(3)	12.907(3)
α (°)	76.39(3)	101.62(3)
β (°)	78.81(3)	100.94(3)
γ (°)	66.84(3)	98.19(3)
V (Å^3)	1178.7(5)	1071.8(4)
Z	1	2
ρ_{calc} (Mg m^{-3})	1.642	1.893
μ (mm^{-1})	1.211	2.178
Maximum, minimum transition	0.83, 0.83	0.938, 0.812
Index ranges	$-11 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 13$, $-19 \leqslant l \leqslant 13$	$-9 \leqslant h \leqslant 9$, $-11 \leqslant k \leqslant 11$, $-14 \leqslant l \leqslant 14$
θ (°)	4–27	2–24
T (K)	150	150
F(000)	594	612
Reflections collected	7469	5363
Independent reflections (R_{int})	7469 [0.036]	3203 [0.082]
Data/restraints/parameters	7446/99/632	3203/0/319
Goodness-of-fit (GOF) on F^2	0.9905	0.992
Final R indices [$I > 2\sigma(I)$] R_1, wR_1	0.0578, 0.1376	0.0716, 0.1672
R indices (all data) R_1, wR_1	0.0669, 0.1464	0.1217, 0.2111
Absolute structural parameters	0.08(2)	n.d.
Largest res. (e Å^{-3})	1.33 and −1.38	1.272 and −0.764

928 (m), 797 (m), 752 (s), 702 (s), 671 (s), 621 (s), 546 (m), 480 (w). ES-MS: m/z (%) = 427.01 [Cu(Ph-Pyox)(MeCN)(ClO_4)]$^+$ (100), 409.05 [Cu(Ph-Pyox)(2-Py-CO_2)]$^+$ (24), 385.98 [Cu(Ph-Pyox)(ClO_4)]$^+$ (13); HR ES-MS for [Cu(Ph-Pyox)(MeCN)(ClO_4)]$^+$: m/z = 426.9985 calc. for $C_{16}H_{15}ClCuN_3O_5$: 426.9996). UV–Vis (MeCN): λ_{max} (ε dm^{-3} mol^{-1} cm^{-1}) = 695 nm (46.9). *Anal.* Calc. for $C_{14}H_{12}Cl_2CuN_2O_9$: C, 34.55; H, 2.49; N, 5.76. Found: C, 34.79; H, 2.69; N, 5.77%.

2.3.4. *[Cu(^{i}Pr-Pyox)(NCMe)$_2$(ClO_4)$_2$] (2c)*

IR data (KBr pellet, cm^{-1}): 3411 (br), 3326 (m), 3260 (m), 3195 (m), 3069 (m), 2964 (m), 2924 (w), 2869 (w), 2069 (w), 2019 (w), 1652 (s), 1596 (s), 1571 (m), 1501 (w), 1471 (w), 1415 (m), 1300 (w), 1260 (m), 1144 (s), 1109 (s), 1093 (s), 1018 (m), 927 (m), 802 (m), 757 (w), 666 (w), 625 (s), 475 (w). ES-MS: m/z (%) = 393.02 [Cu(^{i}Pr-Pyox)(MeCN)(ClO_4)]$^+$ (100), 375.07 [Cu(^{i}Pr-Pyox)(2-Py-CO_2)]$^+$ (71), 542.10 [Cu(^{i}Pr-Pyox)$_2$(ClO_4)]$^+$ (32), 351.99 [Cu(^{i}Pr-Pyox)(ClO_4)]$^+$ (29); HR ES-MS for [Cu(^{i}Pr-Pyox)(MeCN)(ClO_4)]$^+$: m/z = 393.0163 (calc. for $C_{13}H_{17}ClCuN_3O_5$: 393.0153). UV–Vis (MeCN): λ_{max} (ε dm^{-3} mol^{-1} cm^{-1}) = 693 nm (49.6). *Anal.* Calc. for $C_{11}H_{14}Cl_2CuN_2O_9$: C, 29.19; H, 3.12; N, 6.19. Found: C, 29.05; H, 3.35; H, 6.48%.

2.4. Oxidation catalysis

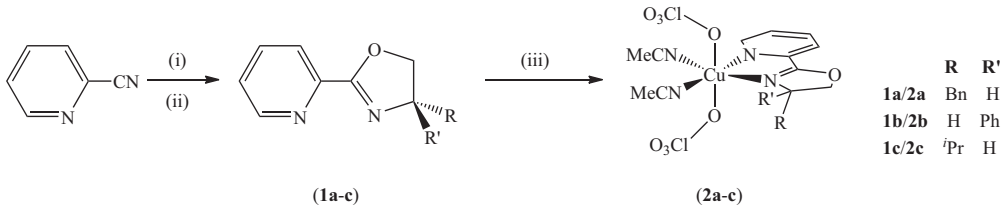
A solution of the ligand (0.05 mmol) and Cu salt (0.04 mmol) in dry acetonitrile (3 ml) were stirred at room temperature for 1 h to ensure formation of the copper complex. Cyclohexene (5 mmol) was then added. A solution of *tert*-butyl peroxybenzoate (0.85 mmol) in acetonitrile (2 ml) was added. After the reaction was judged to be complete (TLC: disappearance of the peroxyester) the solvent was removed under reduced pressure and the residue dissolved in dichloromethane (20 ml). The solution was washed successively with 10% aqueous $NaHCO_3$, brine, and water, and dried over Na_2SO_4. Evaporation of the volatiles and purification by flash chromatography (silica, hexane/ethyl acetate 50:1) afforded the allylic benzoate. The enantiopurities were determined by chiral HPLC using a Chiracell OJ column [hexane; flow rate 0.35 ml min^{-1}; t_1 = 36.2 min (*R*), 38.9 min (*S*)].

2.5. Crystallographic studies

Crystals of **2a** suitable for X-ray diffraction were grown by the slow evaporation of a saturated acetonitrile solution (50 mg in 10 ml) over a period of 7 days. During the crystallisation, crystals of **3** were formed alongside those of **2a**. Diffraction data, using Mo-Kα radiation, were collected at low temperature on a Nonius Kappa-CCD diffractometer. A semi-empirical absorption correction was applied. The structures were solved by direct methods and refined using full matrix least squares methods. Hydrogen atoms were input at calculated positions and refined with the riding model. The calculations were performed using SIR92 [13], SIR97 [14], CRYSTALS [15] and SHELX [16]. Crystal and experimental data are provided in Table 1. The crystals of both **2a** and **3** were poorly diffracting and therefore show low completeness values, although the data: parameter ratios were acceptable. Structure solution and refinement proceeded without any adverse effects and gave reliable molecular information. Complex **3** has been previously prepared by an alternative route, as discussed below.

2.6. DFT calculations

DFT calculations were carried out using the Gaussian 09 package [17]. Geometry optimisations were performed at the B3LYP level [18,19], with the 6-31+G(d,p) basis set on all atoms [20–23]. Time-dependent DFT (TD-DFT) calculations also employed B3LYP. As shown by Vlček et al. [24], solvent effects can be crucial for obtaining satisfactory agreement between experiment and TD-DFT. Solvent was therefore modelled using the polarisable continuum model [25], with the molecular cavity defined by a united atom model that incorporates hydrogen into the parent heavy atom, and included in both geometry optimisations and TD-DFT



Scheme 1. Preparation of pyridine oxazoline (Pyox) ligands and complexes. Reagents: (i) EtOH/Na; (ii) $H_2NC(R)(R')CH_2OH$, $CHCl_3$, (iii) $Cu(ClO_4)_2$, MeCN.

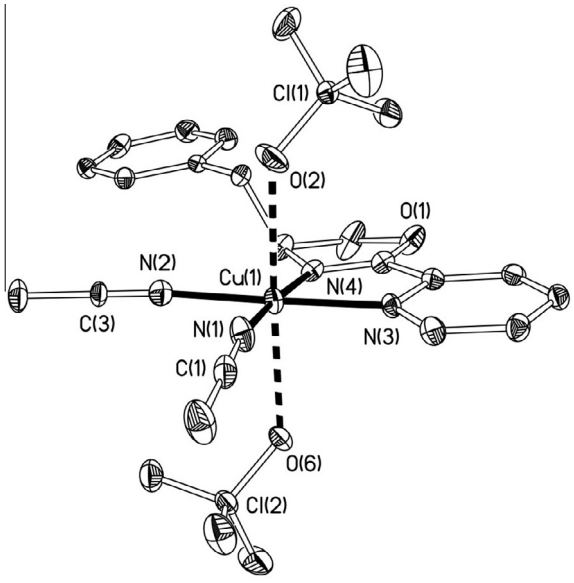


Fig. 1. Molecular structure of **2a**. Ellipsoids are drawn at 25% probability and H atoms are omitted for clarity.

calculations. Triplet states were confirmed not to suffer from significant spin contamination *via* the expectation value of the S^2 operator, which in all cases were less than 0.76. Thus, effects of spin-contamination on energy differences and optimised structures are expected to be negligible.

3. Results and discussion

3.1. Synthesis and characterisation

The pyridine-oxazoline ligands R-Pyox (R = Bn **1a**, Ph **1b**, ^{i}Pr **1c**) were prepared by coupling amino alcohols with 2-cyanopyridine *via* a Pinner reaction (Scheme 1), following the method of Brunner and Obermann [3]. Since our interests are concerned with the catalytic applications of these ligands with copper, the Cu(II) complexes [Cu(R-Pyox)$(NCMe)_2(ClO_4)_2$] (R = Bn **2a**, Ph **2b** and ^{i}Pr **2c**) were prepared by reacting the appropriate ligand with [Cu$(H_2O)_6][ClO_4]_2$ in acetonitrile solution (Scheme 1). The copper complexes **2a–c** were obtained as pale blue solids upon concentration of the reaction mixture. The complexes were characterised by IR and UV–Vis spectroscopies, mass spectrometry (including HR), along with X-ray crystallography and EPR spectroscopy for complex **2a**.

The UV/vis spectra of complexes **2a–c** exhibited only a slight variation in maxima and molar absorption coefficient with alterations in stereodirecting group. Given that the TD-DFT calculations suggest little contribution of this group to the principal excited states (*vide infra*), this is expected, and consistent with a common coordination chemistry for each of the three ligand derivatives. Contrary to expectations, the infrared spectra of the bulk material, isolated by removal of the volatiles under reduced pressure, did not display the expected ν(C≡N) stretches. Furthermore, no identifiable ions could be detected in the electrospray mass spectra when using the isolated material, which was dissolved in acetonitrile immediately prior to data collection. Mass spectra measurements using the *in situ* prepared samples (*i.e.* using the reaction mixture without prior removal of the volatiles), gave spectra in which the ions attributed to $[Cu(R\text{-}Pyox)(NCMe)_n(ClO_4)]^+$ ($n = 0$ or 1) were clearly visible, and upon which accurate mass data were obtained. Spectra recorded using the isolated material, and which had been dissolved in acetonitrile for several hours before data acquisition, showed identical signals to those observed from the *in situ* prepared samples. These data suggest that the coordinated acetonitrile is highly labile, and is easily removed *in vacuo*. The precise nature of the resulting coordination complex is unclear, but we note that there was no evidence of bis(Pyox) complex formation (*e.g.* $[Cu(R\text{-}Pyox)_2(ClO_4)_2]$); more detailed analysis of these species was not possible, since the acetonitrile-free species were found to be insoluble in all solvents except for acetonitrile, which necessarily re-formed $[Cu(R\text{-}Pyox)(NCMe)_2(ClO_4)_2]$ over time. Combustion elemental analysis data were irreproducible, and were consistent with a varying, non-stoichiometric amount of acetonitrile, unless the samples were dried *in vacuo* for an extended period of time to a vacuum of 1×10^{-2} mbar. In such cases, elemental analyses were consistent with the expected complex but without the coordinated acetonitrile, *i.e.* $[Cu(R\text{-}Pyox)][ClO_4]_2$. Attempts to prepare complexes bearing *two* Pyox ligands, $[Cu(R\text{-}Pyox)_2(ClO_4)_2]$, by adding an excess of the Pyox ligands to the reaction mixtures, yielded only complexes **2a–c**.

3.2. X-ray crystallography

The structure of the complexes was confirmed by single crystal X-ray analysis of [Cu(Bn-Pyox)$(NCMe)_2(ClO_4)_2$] **2a**. The perchlorate

Table 2
Selected bond lengths (Å) and angles (°) for **2a**. Values for the second crystallographically independent molecule are provided in parentheses.

Cu(1)—O(2)	2.487(7) [2.510(5)]	Cu(1)—N(2)	2.019(7) [1.964(7)]
Cu(1)—O(6)	2.426(5) [2.433(6)]	Cu(1)—N(3)	2.021(6) [2.023(6)]
Cu(1)—N(1)	1.995(8) [1.975(7)]	Cu(1)—N(4)	1.972(7) [1.972(6)]
N(1)—Cu(1)—N(2)	90.8(3) [91.0(3)]	O(2)—Cu(1)—O(6)	173.5(3) [175.3(2)]
N(1)—Cu(1)—N(3)	92.6(3) [92.4(3)]	Cu(1)—N(1)—C(1)	165.4(8) [167.3(6)]
N(2)—Cu(1)—N(4)	94.9(3) [95.2(3)]	Cu(1)—N(2)—C(3)	174.8(7) [166.1(7)]
N(3)—Cu(1)—N(4)	81.6(3) [81.4(3)]		

anion was utilised in order to aid crystallisation. The molecular structure is depicted in Fig. 1, with principal bond lengths and angles provided in Table 2.

The asymmetric unit of the structure contains two symmetry independent molecules that are related by a pseudocentre of inversion; the difference between the two molecules is manifested in the relative orientation of the perchlorate anions relative to the Pyox and acetonitrile ligands. A comparison of the two structures is provided in Fig. S1 in the supplementary information. The equivalent metric parameters show no significant differences. The copper assumes a distorted octahedral geometry, with two acetonitrile ligands coordinated in a mutually *cis* arrangement, forming an approximate square plane with the Pyox ligand {sum of angles subtended at Cu in the equatorial plane: 359.9(12)°}. Two perchlorate ligands occupy the axial positions, and exhibit elongated Cu-O bond lengths, as expected for the Jahn–Teller distorted d^9 copper centre. The Cu—$O_{perchlorate}$ bond lengths of 2.426(5) and 2.487(7) are well within the sum of the van der Waals radii (2.92 Å) [26], and are comparable with copper-coordinated perchlorate ligands in the Cambridge Structural Database (mean Cu—O distance: 2.53 Å) [27]. The bond lengths associated with the Pyox ligand and acetonitrile ligands are unremarkable. Interestingly, the coordination of the acetonitrile ligands deviate significantly from the expected linear arrangement: the angle subtended at N(1) and N(2) being 165.4(8)° and 174.8(7)° respectively. It is noteworthy that the greatest deviation from linear occurs in the acetonitrile furthest away from the Pyox stereodirecting group, which may be expected to be closer to 180° based upon steric arguments. We note however that the difference is negligible in the crystallographically independent molecule {167.3(6) and 166.1(7) respectively}, and that deviations from linear coordination of nitriles is not uncommon, with the Cu—N—C angle in the structurally related [Cu(bpy)$(NCMe)_2(ClO_4)_2$] being 169.7° [28] and the mean M-N-C angle in the Cambridge Structural Database being 169.8° (5052 examples of transition metal-nitrile complexes). Given that the spectroscopic data are consistent across the series of complexes, we propose that the molecular structure of **2a** shown in Fig. 1 is likely to be similar to the structures of **2b** and **2c**.

Alongside the crystals of **2a**, several distinctly different crystals were formed. The serendipitous formation of these crystals provides a clear insight into the stability of these Pyox ligands in the coordination sphere of copper(II).

This second species, **3**, is a supramolecular array of copper, ligated by 2-pyridinecarboxylate ligands. The pyridine carboxylate moieties are presumably formed by the *in situ* hydrolysis of the Pyox ligands (Scheme 2) in the presence of Cu(II). This structure has previously been reported from the reaction of Cu(II) salts with

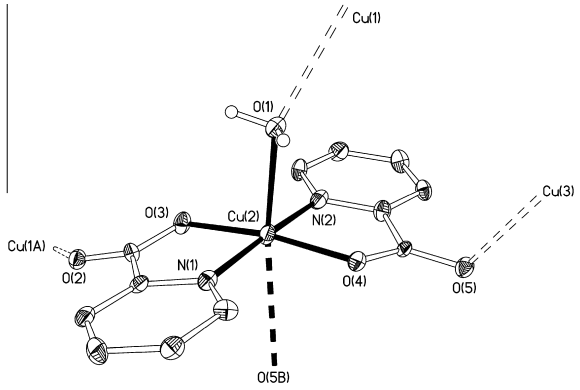
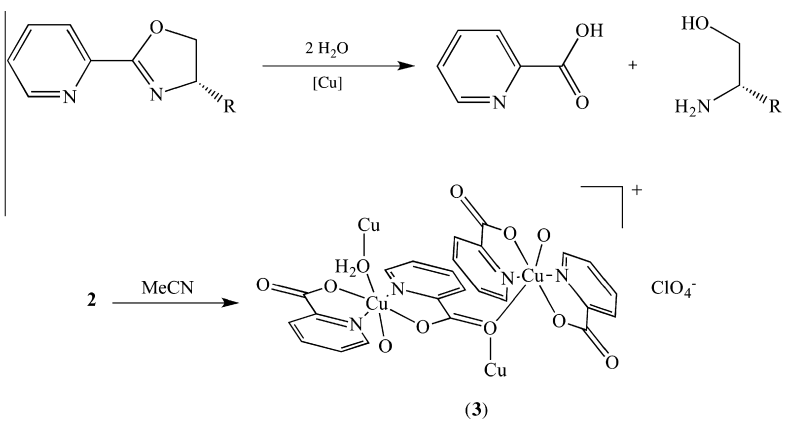


Fig. 2. Molecular structure of **3**. Probability ellipsoids are drawn at 25%. H atoms (other than those associated with the coordinated water molecule) and perchlorate counterion are omitted for clarity. Only one copper environment is shown.

Table 3
Principal bond lengths (Å) and angles (°) for **3**. Atoms labelled with suffixes A–E are related by symmetry elements as follows: A = −*x*, *y*, 1−*z*; B = *x*, *y*−1, *z*; C = *x*−1, *y*, *z*; D = 1−*x*, −1−*y*, 1−*z*; E = 1−*x*, −*y*, 1−*z*.

Cu(1)—O(7A)	1.940(7)	Cu(2)—O(4)	1.942(7)
Cu(1)—O(7B)	1.940(7)	Cu(2)—O(3)	1.982(7)
Cu(1)—O(2C)	1.957(7)	Cu(2)—N(1)	1.984(9)
Cu(1)—O(2D)	1.957(7)	Cu(2)—N(2)	1.987(9)
Cu(1)—O(1)	2.644(7)	Cu(2)—O(1)	2.368(7)
Cu(3)—N(3A)	1.978(8)	Cu(2)—O(5E)	2.735(7)
Cu(3)—N(3)	1.978(8)	Cu(3)—O(5)	2.332(7)
Cu(3)—O(6)	1.989(7)	Cu(3)—O(5A)	2.332(7)
Cu(3)—O(6A)	1.989(7)		
O(7)—Cu(1)—O(7B)	180.0	O(2C)—Cu(1)—O(2D)	180.0
O(7A)—Cu(1)—O(2C)	95.9(3)	O(7A)—Cu(1)—O(1)	102.2(3)
O(7B)—Cu(1)—O(2C)	84.1(3)	O(7B)—Cu(1)—O(1)	77.8(3)
O(7A)—Cu(1)—O(2D)	84.1(3)	O(2C)—Cu(1)—O(1)	97.6(3)
O(7B)—Cu(1)—O(2D)	95.9(3)	O(2D)—Cu(1)—O(1)	82.4(3)
O(4)—Cu(2)—N(1)	97.0(3)	O(4)—Cu(2)—N(2)	83.9(3)
O(3)—Cu(2)—N(1)	82.6(3)	O(3)—Cu(2)—N(2)	95.8(3)
N(1)—Cu(2)—N(2)	175.56(3)	O(4)—Cu(2)—O(5E)	77.5(3)
O(3)—Cu(2)—O(4)	170.6(3)	O(3)—Cu(2)—O(5E)	93.2(3)
O(1)—Cu(2)—O(4)	88.9(3)	N(1)—Cu(2)—O(5E)	77.1(3)
O(1)—Cu(2)—O(3)	100.5(3)	N(2)—Cu(2)—O(5E)	98.8(3)
N(1)—Cu(2)—O(1)	93.4(3)	O(3)—Cu(2)—O(5E)	162.2(2)
N(2)—Cu(2)—O(1)	91.1(3)	N(3A)—Cu(3)—N(3)	180.0
N(3A)—Cu(3)—O(6)	96.8(3)	O(6)—Cu(3)—O(5)	91.4(3)
N(3)—Cu(3)—O(6)	83.2(3)	O(6A)—Cu(3)—O(5)	88.6(3)
N(3A)—Cu(3)—O(6A)	83.2(3)	N(3A)—Cu(3)—O(5A)	88.1(3)
N(A)—Cu(3)—O(6A)	96.8(3)	N(3)—Cu(3)—O(5A)	91.9(3)
O(6)—Cu(3)—O(6A)	180.0	O(6)—Cu(3)—O(5A)	88.6(3)
N(3A)—Cu(3)—O(5)	91.9(3)	O(6A)—Cu(3)—O(5A)	91.4(3)
N(3)—Cu(3)—O(5)	88.1(3)	O(5)—Cu(3)—O(5A)	180.0



Scheme 2. Copper-catalysed ligand hydrolysis.

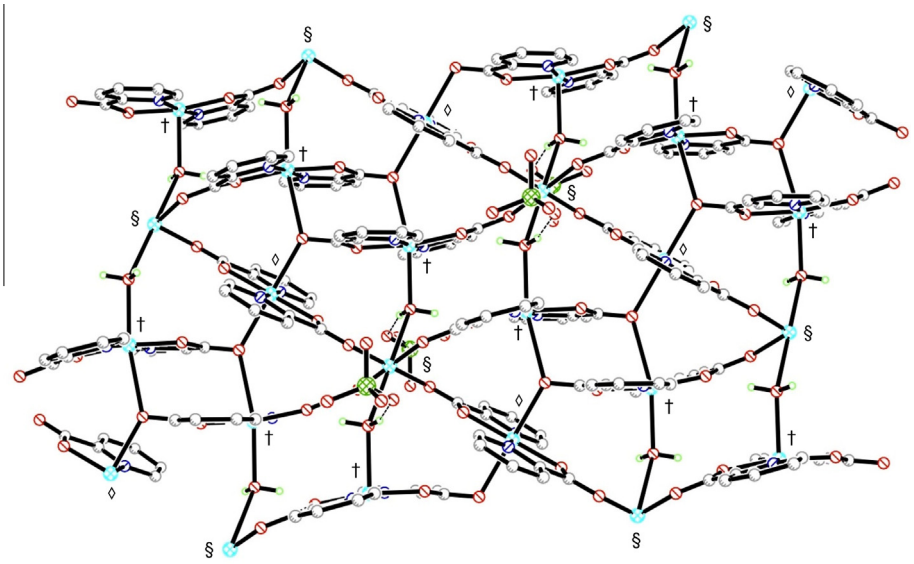


Fig. 3. Packing diagram of **3**. H atoms (other than those associated with the coordinated water molecule) are omitted for clarity. § = Cu(1), † = Cu(2), ◇ = Cu(3).

picolinic acid [30]; its formation in this instance is interesting because it implicates ligand stability in an assessment of catalytically active complexes. The hydrolysis of bis(hydroxymethyl) substituted Pyox ligands (affording pyridine-2-carboxylate and the corresponding amino alcohol) has been reported by Segl'a and co-workers [29], although only in aqueous solution under forcing conditions; complex **3** is interesting in that it was formed under much milder conditions, presumably with water arising from the use of a hydrated copper perchlorate salt. A fragment of the asymmetric unit is depicted in Fig. 2, with principal bond lengths and angles given in Table 3, although the full details of the supramolecular structure are best appreciated from the extended structure shown in Fig. 3.

Each copper(II) ion occupies an octahedral coordination geometry. There are three distinct copper environments, with two of the copper centres – Cu(2) and Cu(3) – bound by two bidentate 2-pyridylcarboxylate ligands which coordinate *via* the pyridyl nitrogen and one of the carboxylate oxygens; the remaining carboxylate oxygen coordinates to a different copper centre, which gives rise to the observed two-dimensional polymeric structure. Cu(1) and Cu(2) are bridged by a water molecule; this water molecule partakes in hydrogen bonding to the perchlorate anion {O(1)—H(11)···O(9)} which are located in a regular array on either side of the sheet structure. The coordination geometry about Cu(1) is more significantly distorted from ideal octahedral than Cu(2) and Cu(3).

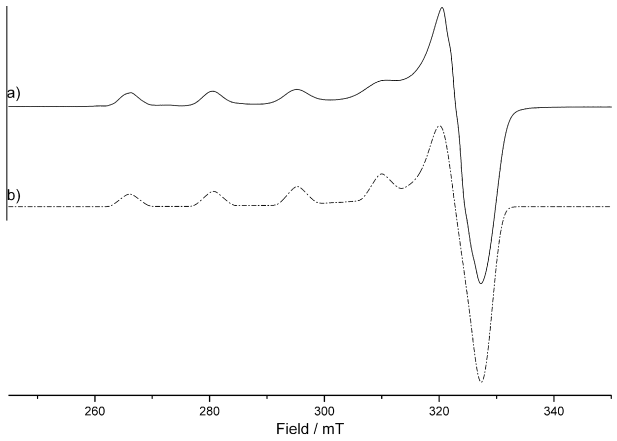


Fig. 4. X-band CW EPR spectrum (140 K) of **2a**. (a) Experimental, (b) simulation.

3.3. EPR spectroscopy

To gain further information on the structure and coordination of the complex, the low temperature (140 K) CW-EPR spectrum of **2a** was recorded (Fig. 4). The spectrum was simulated using a quasi-axial g tensor ($g_1 = 2.075 \pm 0.005$, $g_2 = 2.078 \pm 0.005$, $g_3 = 2.328 \pm 0.005$), with ^{63,65}Cu hyperfine determined from the simulation as $^{Cu}A_1 = 30 \pm 7$ MHz, $^{Cu}A_2 = 30 \pm 7$ MHz and $^{Cu}A_3 = 409 \pm 4$ MHz. The spectrum is considerably broadened, particularly in the $g_{1,2}$ region, presumably due to the underlying ^{14}N superhyperfine couplings from the Pyox ligand. There is also some evidence of g/A strain in the spectrum (particularly in the $m_{Cu} = -3/2$ line). The hyperfine couplings were determined from the simulation as $^{Cu}A_1 = 30 \pm 7$ MHz, $^{Cu}A_2 = 30 \pm 7$ MHz, $^{Cu}A_3 = 409 \pm 4$ MHz, and $^{N}A_1 = 30 \pm 7$ MHz, $^{N}A_2 = 30 \pm 7$ MHz, $^{N}A_3 = 38 \pm 4$ MHz based on two equivalent ^{14}N nuclei. Although the ^{N}A hyperfine values cannot be resolved, the expected coupling magnitude of ~30 MHz (as limited by the measured EPR linewidth) is consistent with those expected for Cu(II) complexes coordinated to N_4, N_2O_2 and N_2 bearing ligands (*i.e.* in porphyrins, [31] salens, [32] bisoxazolines [33]). [34] To date, there are no detailed EPR studies reported for Cu(II)–Pyox complexes. However Bolm et al. described the EPR, ENDOR and HYSCORE analysis of a series of Cu(II) bis-sulfoxime complexes, whereby the bidentate ligand coordinated to Cu(II) *via* the two nitrogens, and both solvent molecules and counterions were also involved in the copper coordination sphere. The reported g/A values [35] are similar for **2a**. The coordinated acetonitrile and perchlorate are not directly evident from the EPR measurements, but the g and ^{Cu}A values are typical of those expected for a distorted 6-coordination mode for the Cu(II) ion, and thus consistent with the structure reported in Fig. 1. The interactions with the two Pyox nitrogen nuclei, and potentially the coordinated acetonitrile ligand, could be further probed *via* high-frequency ENDOR measurements (data unavailable).

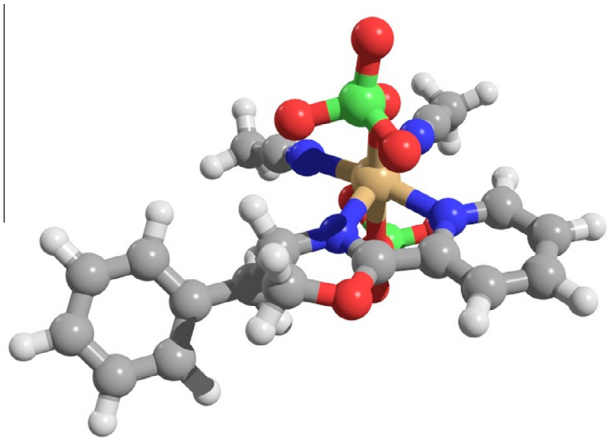
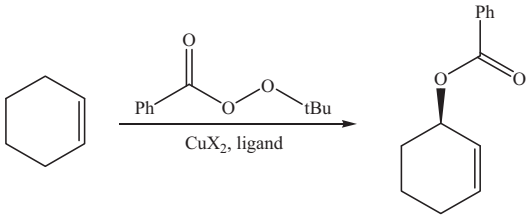


Fig. 5. Calculated structure of [Cu(Bn-PyOx)$(NCMe)_2(ClO_4)_2$].

3.4. DFT calculations

As a representative example, the structure of **2a** was calculated using density functional methods. The calculated structure is provided in Fig. 5; the metric parameters are in reasonable agreement with those obtained from the X-ray structure (*vide infra*). The Cu—N bond lengths are around 2 Å, which are similar to those in **2a**, whilst the Cu—$O_{perchlorate}$ distances are 2.503 and 2.255, in which the latter is somewhat underestimated and the former is in excellent agreement with the experimental data. Interestingly, a calculated structure that reproduced the perchlorate coordination was only obtained upon using diffuse functions to the basis set (6-31+G(d,p)); varying the functional to B3PW91 or M06, or the basis set to 6-311+G(d,p) or aug-cc-pVDZ, did not significantly alter the Cu—$O_{perchlorate}$ distances. Equivalent calculations performed employing the 6-31G(d,p) basis set gave 5-coordinate structures in which one perchlorate was de-coordinated from the metal.

TD-DFT calculations were performed on the optimised structure, and indicated excited state absorptions at 709 and 693 nm, in agreement with the observed spectral absorption at 694 nm. These absorptions correspond largely to transitions between the HOMO-11 and the SOMO (Fig. 6), and contain both LMCT and *d-d* character.



Scheme 3. Asymmetric allylic oxidation of cyclohexene.

Table 4
Asymmetric allylic oxidation of cyclohexene using $PhCO_3$-^{t}Bu as oxidant.

Entry	Ligand	Cu salt	T (°C)	Solvent	Time[a]	Conv%	ee (%)[b]
1	**1a**	$Cu(OTf)_2$	20	MeCN	6 weeks	99	29
2	**1b**	$Cu(OTf)_2$	20	MeCN	6 weeks	99	*15*
3	**1c**	$Cu(OTf)_2$	20	MeCN	6 weeks	99	37
4	**1a**	$Cu(OTf)_2$	0	MeCN	6 weeks	0[c]	–
5	**1b**	$Cu(OTf)_2$	0	MeCN	6 weeks	0[c]	–
6	**1c**	$Cu(OTf)_2$	0	MeCN	6 weeks	0[c]	–
7	**1a**	$Cu(OTf)_2$	20	Acetone	6 weeks	23	<5
8	**1b**	$Cu(OTf)_2$	20	Acetone	6 weeks	99	<5
9	**1c**	$Cu(OTf)_2$	0	Acetone	6 weeks	54	<5
10	–	$Cu(OTf)_2$	20	MeCN	2 weeks	99	<2
11	–	$Cu(OTf)_2$	0	MeCN	6 weeks	99	<2
12	**1a**	$Cu(OTf)_2$	20	MeCN[d]	3 weeks	45	25
13	**1b**	$Cu(OTf)_2$	20	MeCN[d]	3 weeks	64	*16*
14	**1c**	$Cu(OTf)_2$	20	MeCN[d]	3 weeks	40	26
15	**1a**	$Cu(OTf)_2$	20	Acetone[d]	3 weeks	30	18
16	**1b**	$Cu(BF_4)_2$	20	Acetone[d]	3 weeks	31	*10*
17	**1c**	$Cu(OTf)_2$	20	Acetone[d]	3 weeks	60	12
18	**1a**	$Cu(OTf)_2$	20	MeCN[e]	4 weeks	53	30
19	**1b**	$Cu(OTf)_2$	20	MeCN[e]	4 weeks	41	*15*
20	**1c**	$Cu(OTf)_2$	20	MeCN[e]	4 weeks	65	35

[a] Reactions were run until judged complete by TLC (disappearance of the peroxyester).
[b] The *R* enantiomer is predominant except for values in italics, for which the *S* enantiomer is predominant, based upon previous reports [39].
[c] No reaction was observed under these conditions.
[d] 1 eq. of phenylhydrazine added.
[e] Catalysis performed under argon in anhydrous solvent.

3.5. Oxidation catalysis

The use of pyridine-oxazoline ligands in the copper-catalysed allylic oxidation of cyclic alkenes was reported by Clark [4], who employed $[Cu^I(NCMe)_4][PF_6]$ as the copper source and several ligand motifs, including **1b**. It was reported that the oxidation reaction was sluggish at room temperature, an observation supported

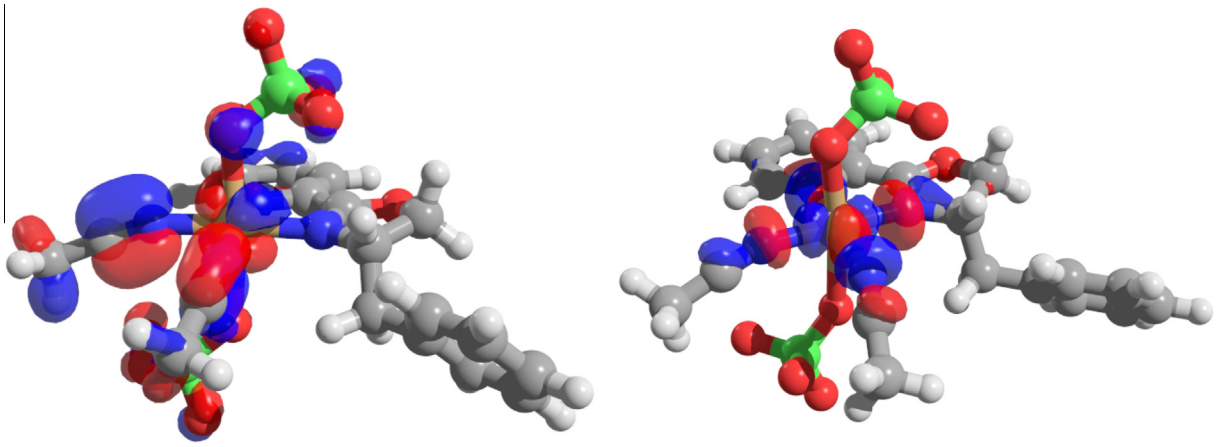


Fig. 6. Principal β-MOs involved in TD-DFT computed absorption (HOMO-11 → SOMO).

by others with copper bisoxazoline complexes [36]. Out of the various pyridine-oxazoline ligand types employed by Clark, those containing the pyridine directly bound to the oxazoline moiety were found to give the lowest enantioselectivities (17% and 28% for Ph and ^{i}Bu stereodirecting groups respectively).

Copper Pyox complexes were probed for their effectiveness in the copper-catalysed allylic oxidation of cyclohexene with *tert*-butyl peroxybenzoate, using 5 mol% catalyst (Scheme 3) [37,38]. Owing to the ambiguity of the coordination chemistry (specifically in the formation of **3**), we prepared samples for catalytic studies *in situ*, immediately prior to adding the catalytic substrates. The catalyst performances are summarised in Table 4.

When Cu(II) complexes bearing Pyox ligands (triflate analogues of **2a**–**c**) were employed as catalysts, acetonitrile was consistently found to be the most suitable solvent, as is consistent with several other reports. Previous studies of Cu(II) catalysed oxidation reactions with bisoxazoline ligands have shown very little variation in catalytic activity and stereodirection with differing counter ions [39]. When acetone was used as the solvent, no stereoinduction was found with any of the three pre-catalysts. Table 3 includes isolated yields, however for each entry the catalytic reaction was allowed to run until the complete disappearance of the peroxyester. It is noteworthy that this took significantly longer when compared to most other ligand systems, *i.e.* 6 weeks at ambient temperature compared to typically 1 week for bisoxazoline complexes [36] and 2 weeks when no chiral ligand was added (entries 10 and 11). Given the propensity for lower enantioselectivities at elevated temperatures, higher reaction temperatures were not employed, but it was noted that cooling the reaction to 0 °C completely suppressed the reaction, with no conversion being observed after 6 weeks. The ^{i}Pr (**2c**) complex was found to give the highest selectivity (37%, entry 3), with the benzyl congener (**2a**) giving 29% (entry 1). Adding phenylhydrazine has been shown to increase the rates, yields and selectivities in previous studies on bisoxazoline and chiral bipyridyl complexes [40] by reducing the Cu(II) to Cu(I) *in situ*. Here, the reaction rate was increased but the reaction was still found to be slow and enantioselectivities were lower (entries 12–14). Interestingly, whilst using acetone as a solvent gave no enantioselectivity when only Cu(II) was employed (entries 7–9), reactions in acetone were found to give modest enantioselectivities when phenylhydrazine was added (entries 15–17).

Given that the complexes **2a**–**c** are pure (by elemental analysis) when first formed, the afore-mentioned ligand hydrolysis reactions are likely to lead to a gradual increase in the quantity of **3** present in the reaction mixture. It is a reasonable supposition that the 2-pyridine-carboxylate coordinated copper centres may be able to catalyse the reaction, albeit in a non-stereoselective manner. In order to probe this hypothesis, the catalysis studies were repeated using strictly anhydrous conditions (other than drying the peroxyester for safety reasons). In these cases, no alteration in enantioselectivity was observed (entries 18–20); this suggests that the copper-promoted ligand hydrolysis, whilst forming an achiral copper species, does not degrade the enantioselectivity. This suggests that the copper centres incorporated into the coordination polymer are subsequently unavailable for catalytic activity, a conclusion which is qualitatively supported by the observation that the peroxyester was consumed in 4 weeks, rather than 6 weeks under aerobic conditions.

4. Conclusions

Copper complexes of pyridine-oxazoline (Pyox) ligands have been prepared and are suitable catalysts for the allylic oxidation of cyclohexene. However, in the coordination sphere of copper, these ligands show a propensity to undergo hydrolysis, affording 2-pyridine carboxylate ligands, which were isolated as part of a coordination polymer with the copper(II) ions. This observation suggests that this process may be an important contributor in other systems containing oxazoline ligands; ligand stability during catalysis is often neglected and an understanding of these processes will be beneficial in the rational design of catalytically active, functional metal complexes.

Acknowledgements

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Appendix A. Supplementary material

CCDC 886430 and 886431 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2015.10.032. The data supporting the results presented in this article are freely available via the Cardiff University data catalogue at http://dx.doi.org/10.17035/d.2015.100130.

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