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Introduction

Small molecule complexes employing redox active transitionmetal ions and pro-radical ligands provide significant insight into the complexity of a number of metalloenzyme processes.^{1,2} Researchers have harnessed the redox activity of tyrosine ligands to develop catalysts for multi-electron catalysis.³⁻¹⁴ The metalloenzyme galactose oxidase (GOase) is an important example, which catalyzes the oxidation of p-galactose and a wide range of primary alcohols with concomitant reduction of dioxygen to hydrogen peroxide.^{2,15} The GOase active site contains a cysteine-modified phenol moiety Tyr 272 (Y₂₇₂) and a phenol group of tyrosine 495 (Y₄₉₅)

Synthesis, characterization and catalytic activity of copper(II) complexes containing a redox-active benzoxazole iminosemiquinone ligand†

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A tridentate benzoxazole-containing aminophenol ligand HL^{BAP} was synthesized and complexed with Cu^{II} . The resulting Cu^{II} complexes were characterized by X-ray, IR, UV-vis-NIR spectroscopies, and magnetic susceptibility studies, demonstrating that the ligand is oxidized to the *o*-iminosemiquinone form $[L^{BIS}]^-$ in the isolated complexes. $L^{BIS}Cu^{II}Cl$ exhibits a distorted tetrahedral geometry, while $L^{BIS}Cu^{II}OAc$ is square pyramidal. In both solid state structures the ligand is coordinated to Cu^{II} *via* the benzoxazole, as well as the nitrogen and oxygen atoms from the *o*-iminosemiquinone moiety. The chloride, or acetate group occupies the fourth and/or fifth positions in $L^{BIS}Cu^{II}Cl$ and $L^{BIS}Cu^{II}OAc$, respectively. Magnetic susceptibility measurements indicate that both complexes are diamagnetic due to antiferromagnetic coupling between the d⁹ Cu^{II} centre and iminosemiquinone ligand radical. Electrochemical studies of the complexes demonstrate both a quasi-reversible reduction and oxidation process for the Cu complexes. While $L^{BIS}Cu^{II}X$ (X = CI) is EPR-silent, chemical oxidation affords a species with an EPR signal consistent with ligand oxidation to form a d⁹ Cu^{II} iminoquinone species. In addition, chemical reduction results in a Cu^{II} centre most likely bound to an amidophenoxide. Mild and efficient oxidation of alcohol substrates to the corresponding aldehydes was achieved with molecular oxygen as the oxidant and $L^{BIS}Cu^{II}X-Cs_2CO_3$ as the catalyst.

coordinated to a Cu^{II} center. This enzyme has inspired researchers to design and study small-molecule models capable of efficient alcohol oxidation under mild conditions.^{15–21} Copper complexes employing non-innocent catecholate and semiquinone ligands have also been identified as exhibiting GOase-like reactivity (Scheme 1).²²



Scheme 1 Redox states of GOase.²²

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[†]Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF format, DFT-computed metrical parameters, cyclic voltammograms, and ¹H NMR spectra. CCDC 899392 (L^{BIS}Cu^{II}Cl) and 899393 (L^{BIS}Cu^{II}OAc). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt00004d



Scheme 2 The structure of HL^{BAP}.

Significant efforts have been made towards the synthesis of Cu^{II} complexes containing redox active ligands.²³⁻²⁵ These complexes have provided a platform to study both the magnetic interaction between the d⁹ Cu^{II} center and the radical ligand Tyr 272 (Y_{272}) , and the role of the radical ligand in catalysis. One of the most common classes of redox active ligands are based on o-aminophenols. Metal complexes of this ligand have been studied in the amidophenoxide, iminosemiquinone, and iminoquinone redox states, and certain compounds have shown promise as catalysts.²⁶⁻³¹ Specifically, copper complexes of this ligand act as catalysts for alcohol oxidation, closely following the reactivity of GOase. Thus, these metal complexes models of metalloenzymes such can serve as as GOase.^{28,29,32-34} In addition, metal complexes of phenoxazines and benzoxazoles have proven very useful as catalysts for allylic substitutions, Heck reactions, hydrosilylations, cyclopropanations and Diels-Alder additions.³⁵⁻⁵⁶ Herein, we report the synthesis, characterization, magnetic and redox properties of L^{BIS}Cu^{II}OAc and L^{BIS}Cu^{II}Cl complexes of the newly synthesized [N₂O]-donor benzoxazole ligand (HL^{BAP}, Scheme 2). In addition, we describe the mild and efficient oxidation of alcohols to aldehydes with oxygen as the oxidant and $L^{\rm BIS} C u^{\rm II} X \text{--}$ Cs_2CO_3 as the catalyst-base.

Experimental section

Materials and methods

All chemicals and solvents were purchased from Merck and used without further purification. Manipulations were performed under aerobic conditions using chemicals and solvents as received. 3,5-DTBQ (3,5-di-tert-butylcyclohexa-3,5-diene-1,2dione) was synthesized according to a modified literature procedure.⁵⁷ Electronic spectra were obtained on a Cary 5000 spectrophotometer with a custom-designed immersible fiberoptic quartz probe with variable path length (1 and 10 mm; Hellma, Inc.). Constant temperatures were maintained by a dry ice/acetone bath. Solvent contraction was accounted for in all variable-temperature studies. IR spectra were recorded in the solid state on a FT-IR Bruker Vector 22 spectrophotometer in the 400-4000 cm⁻¹ range. NMR spectra were recorded at 400 MHz on a Bruker DRX spectrometer in CDCl₃ solution. The chemical shifts were referred to TMS using the residual signals from the solvent. Cyclic voltammetry (CV) was performed on a PAR-263A potentiometer, equipped with a Ag wire reference electrode, a glassy carbon working electrode, and a

Pt counter electrode with 0.1 M NBu₄ClO₄ solutions in CH₂Cl₂. Ferrocene was used as an internal standard. Mass spectra (positive ion) were obtained on an Agilent 6210 TOF ESI-MS instrument. The magnetic measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL between 1.8 and 290 K with a dc applied field of 1000 Oe. Measurements were performed on polycrystalline samples of 23.86 and 35.21 mg for L^{BIS}Cu^{II}Cl and L^{BIS}Cu^{II}OAc, respectively. The data sets were corrected for the diamagnetic response in the samples and sample holders. All EPR spectra were collected using a Bruker EMXplus spectrometer operating with a premiumX X-band (~9.5 GHz) microwave bridge. Low temperature measurements of frozen solutions used a Bruker helium temperature-control system and a continuous flow cryostat. Samples for X-band measurements were placed in 4 mm outer-diameter sample tubes with sample volumes of ~300 µL. EPR spectra were simulated with EasySpin 3.1.7 software.58

Synthesis

HL^{BAP}. To a solution of 3,5-DTBO (0.44 g, 2 mmol) in acetonitrile (9 mL) was added 2-aminobenzyl amine (0.122 g, 1 mmol), and the reaction stirred for 4 days at room temperature in the presence of air. The solvent was removed in vacuo, and the green material formed was dissolved in methanoldichloromethane (1:1). After evaporation of the solvent, the brown precipitate was washed with ethanol and dried under vacuum. X-ray quality colorless crystals were grown from a 1:1 solvent mixture of dichloromethane-ethanol. Yield: 0.225 g (40%). Anal. calcd (found) for C₃₅H₄₈N₂O₂: C 79.81 (79.67), H 8.80 (8.61), N 5.32 (5.39). $\nu_{\rm max}$ (KBr)/cm⁻¹: 3415 (O-H), 3258 (N-H), 2959 (C-H), 1595 (C=C), 1474 (C=N), 1047 (C-N), 740 (=C-H bending). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 1.32 (s, 9H), 1.43 (s, 9H), 1.50 (s, 9H), 1.61 (s, 9H), 5.33 (s, 1H), 6.34 (s, 1H), 6.69 (d, 1H), 6.94 (t, 1H), 7.13 (d, 1H), 7.31 (s, 1H), 7.34 (t, 1H), 7.62 (d, 1H), 8.20 (t, 1H), 9.66 (s, 1H). ¹³C{H} NMR (100 MHz, CDCl3): δ 29.60, 30.08, 30.96, 31.67, 31.89, 34.44, 34.55, 35.13, 110.52, 113.76, 114.40, 117.80, 119.53, 122.36, 122.64, 126.68, 128.49, 132.38, 133.55, 135.46, 141.58, 142.32, 145.40, 147.78, 147.83, 149.56, 162.34. m.p. 139-141 °C.

L^{BIS}Cu^{II}OAc. HL^{BAP} (0.525 g, 1 mmol) and triethylamine (0.28 mL, 2 mmol) were dissolved in a 2:1 acetonitriledichloromethane mixture (45 mL), and then Cu(OAc)₂ (0.199 g, 1 mmol) was added. The reaction mixture was stirred for 4 hours at room temperature in the presence of air. X-ray quality blue crystals were grown from a 1:1 solvent mixture of dichloromethane-methanol. Yield: 0.70 g (96%). Anal. calcd (found) for C₃₈H₅₂CuN₃O₄·CH₃CN: C 68.65 (68.34), H 7.32 (7.25), N 4.33 (4.38). ν_{max} (KBr)/cm⁻¹: 2959 (C-H), 1617 (C=C), 1475 (C=N), 1027 (C-N), 802 (=C-H bending). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 1.68 (s, 10H), 1.57 (s, 8H), 1.56 (s, 10H), 1.43 (s, 9H) 2.25 (m, 2H), 2.66 (s, 3H), 3.88 (d, 2H), 5.37 (t, 2H), 6.76 (s, 1H), 7.26 (d, 1H), 8.15 (s, 1H), 9.43 (d, 1H), 10.15 (s, 1H).

 $L^{BIS}Cu^{II}Cl.$ HL^{BAP} (0.525 g, 1 mmol) and triethylamine (0.28 mL, 2 mmol) were dissolved in a 2:1 acetonitrile-

dichloromethane mixture (45 mL), and then CuCl₂·2H₂O (0.17 g, 1 mmol) was added. The reaction mixture was stirred for 4 hours at room temperature in the presence of air. X-ray quality blue crystals were grown from a 1 : 1 solvent mixture of dichloromethane-methanol. Yield: 0.50 g (72%). Anal. calcd (found) for C₃₅H₄₄ClCuN₂O₂: C 66.84 (66.16), H 6.21 (6.13), N 11.14 (10.80). ν_{max} (KBr)/cm⁻¹: 2960 (C-H), 1627 (C=C), 1473 (C=N), 1031 (C-N), 807 (=C-H bending). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 1.15 (s, 9H), 1.43 (s, 9H), 1.51 (s, 19H), 7.10 (s, 1H), 7.38 (s, 1H), 7.62 (q, 2H), 7.92 (d, 1H), 8.25 (s, 2H), 8.32 (s, 1H).

Spectrophotometric chemical redox titrations

Oxidation: under a nitrogen atmosphere at 195 K a 150 μ L aliquot of a CH₂Cl₂ solution of L^{BIS}Cu^{II}Cl (31 mM) was added to 3.0 mL CH₂Cl₂. Monitored by UV-vis-NIR, a solution of [N(C₆H₃Br₂)₃·]⁺SbF₆⁻ in CH₂Cl₂ (2.3 mM) was added in 250 μ L increments resulting in clean conversion to [L^{BIQ}Cu^{II}Cl]⁺.

Reduction: under a nitrogen atmosphere at 195 K a 100 μ L aliquot of a CH₂Cl₂ solution of L^{BIS}CuCl (31 mM) was added to 3.0 mL of PhMe. Monitored by UV-vis-NIR, a solution of CoCp₂ in 30:1 PhMe: CH₂Cl₂ (10 mM) was added in 100 μ L increments resulting in clean conversion to [L^{BAP}CuCl]⁻.

Catalytic activity of $L^{BIS}CuCl$ and $L^{BIS}Cu^{II}OAc$ complexes in alcohol oxidation

Alcohol oxidation experiments were carried out in an oxygen atmosphere at room temperature. In a typical experiment, alcohol (1 mmol), L^{BIS}Cu^{II}Cl (0.024 g, 4 mol%) or L^{BIS}Cu^{II}OAc (0.026 g, 4 mol%) and Cs_2CO_3 (0.650 g, 2 mmol) were stirred in 5 mL of oxygen saturated toluene in a 15 mL two-neck round-bottom flask equipped with an oxygen balloon. The solution was stirred for 6-36 hours, after which the mixture was passed through a syringe filter and was diluted with toluene (2 mL). The progress of the reaction was monitored by gas chromatography. To study the effect of the ligand, a 15 mL two-neck round-bottom flask was charged with CuCl₂ or $Cu(OAc)_2$ and Cs_2CO_3 (0.650 g, 2 mmol) in 5 mL of oxygen saturated toluene. The flask was equipped with an oxygen balloon, and the progress of the reaction was monitored by gas chromatography. To check for the formation of carboxylic acid during the oxidation reaction, the reaction mixture was neutralized with 5% HCl to remove any excess base. After passing through a syringe filter, the sample was dried with sodium sulfate and monitored by gas chromatography.

Calculations

Geometry optimizations were performed using the Gaussian 09 program (Revision A.02),⁵⁹ the B3LYP^{60,61} functional, and the 6-31G(d) basis set on all atoms. Broken-symmetry^{62–64} (BS) DFT calculations were performed with the same functional and basis sets. Frequency calculations at the same level of theory confirmed that the optimized structures were located at a minimum on the potential energy surface. Single point calculations were performed using the B3LYP^{60,61} functional and the TZVP basis set of Ahlrichs^{65,66} on all atoms.

X-ray analysis

Single crystal X-ray crystallographic analysis was performed on a Bruker SMART diffractometer equipped with an APEX II CCD area detector fixed at a distance of 6.0 cm from the crystal and a Mo K α fine focus sealed tube ($\lambda = 0.71073$ nm) operated at 1.5 kW (50 kV, 30 mA) and filtered with a graphite monochromator. Temperature was regulated using an Oxford Cryosystems Cryostream. Suitable crystals were mounted on glass fibers using epoxy as adhesive. The structures were solved using direct methods (SIR92)⁶⁷ and refined by least-squares procedures using CRYSTALS.68 Hydrogen atoms were placed in idealized geometric positions and linked to their respective atoms using a riding model during refinement. The isotropic temperature factor of each hydrogen atom was initially set to 1.2 times that of the atom it is bonded to and then the temperature factors of groups of similar hydrogen atoms were linked during refinement. The *tert*-butyl groups in L^{BIS}Cu^{II}OAc were disordered and modeled accordingly (see CIF file for details). Due to twinning issues, the data for HL^{BAP} could not be refined satisfactorily and so the resulting structure was only used to determine connectivity. Diagrams of L^{BIS}Cu^{II}Cl, L^{BIS}-Cu^{II}OAc, and HL^{BAP} were generated by ORTEP-3 for Windows $(v. 2.00)^{69}$ and rendered using POV-Ray (v. 3.6.1).⁷⁰ For the disordered atoms in L^{BIS}Cu^{II}OAc only the atoms with the higher occupancy are shown. The acetonitrile solvent molecule in L^{BIS}Cu^{II}OAc has not been shown.

Results and discussion

Synthesis and structural characterization of ligand HL^{BAP}

The ligand HL^{BAP} was synthesized *via* the condensation of 2-aminobenzylamine with two equivalents of 3,5-DTBQ. HL^{BAP} was characterized by ¹H and ¹³C NMR spectroscopy (ESI Fig. S1 and S2[†]), IR, elemental analysis, mass spectrometry and X-ray crystallography. The free ligand HL^{BAP} exhibits characteristic IR bands at 1511–1542 cm⁻¹ ($\nu_{C=N}$ stretch), and 3416 cm⁻¹ (ν_{O-H} stretch). Single crystals of HL^{BAP} suitable for X-ray crystallography were obtained by recrystallization from dichloromethane/*n*-hexane. An ORTEP view of the HL^{BAP} ligand is shown in Fig. 1. X-ray analysis shows that the benzox-azole heterocycle forms during the synthesis of the ligand. In



Fig. 1 Molecular structure of HL^{BAP} . H atoms have been omitted for clarity. Thermal ellipsoids are set at 50% probability.⁷¹

addition, a redox-active aminophenolate function is present. Due to the high *R*-value for the structure of HL^{BAP} we were unable to determine the aminophenolate ring bond lengths. However, a ¹H NMR titration of HL^{BAP} using NaOD is consistent with phenolate deprotonation as the pH is raised (ESI Fig.S3[†]). In addition, the ¹H NMR data is consistent with a recent report on a similar ligand system.⁵⁴

Synthesis and structural characterization of $L^{BIS}Cu^{II}X$ complexes

Treating HL^{BAP} with CuCl₂ or Cu(OAc)₂ in the presence of 2 equivalents of Et₃N under aerobic conditions in acetonitrile at 298 K afforded a microcrystalline precipitate of L^{BIS}Cu^{II}Cl and L^{BIS}Cu^{II}OAc, respectively. Elemental analytical data of the complexes corresponds to the calculated values for a 1:1 metal: ligand ratio. In the IR spectra of the complexes, the strong and sharp ν_{O-H} stretch of the ligand disappears, and the $\nu_{C=N}$ band is shifted to lower energy by 10–20 cm⁻¹ as compared to the $\nu_{C=N}$ band of the free ligand. The monomeric complexes isolated herein differ from the dimeric Cu^{II} complex of a similar aminophenol ligand recently reported.⁷² The increased steric bulk of the [L^{BIS}]⁻ ligand used in this work likely restricts dimerization.

X-ray analysis

Blue crystals of the two copper complexes for X-ray analysis were obtained from a methanol-dichloromethane (1:2) mixture. Crystallographic data for both complexes are shown in Table 1. Selected bond distances and angles are listed in Table 2.

Crystal structure of L^{BIS}Cu^{II}Cl

The solid state structure of $L^{BIS}Cu^{II}Cl$ displays a distorted tetrahedral geometry (Fig. 2). The dihedral angle between the planes defined by N[1]-Cu[1]-O[1] and N[2]-Cu[1]-Cl[1] is 50.6° indicating a significant twist in the structure. The Cu^{II}

 Table 1
 Crystallographic data for L^{BIS}Cu^{III}OAc, and L^{BIS}Cu^{III}CI

	L ^{BIS} Cu ^{II} OAc	L ^{BIS} Cu ^{II} Cl
Empirical formula	C ₃₉ H ₅₀ CuN ₃ O ₄	C35H44ClCuN2O2
Formula weight	688.39	623.74
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_{1}/n1$
a (Å)	12.5963(12)	16.4069(18)
b (Å)	16.3407(16)	12.3090(14)
c (Å)	18.3053(18)	17.1757(19)
α (°)	90	90
β(°)	98.1790(10)	110.1470(10)
γ(°)	90	90
$V(A^3)$	3729.5(6)	3256.4(6)
Z	4	4
T (K)	298	150
$\rho_{\text{calcd}} (\text{g cm}^{-3})$	1.226	1.272
$\mu (\text{mm}^{-1})$	0.627	0.785
Reflections collected	44 491	35 679
Significant reflections	6148	7055
$R[I > 2.5\sigma(I)]$	0.0417	0.0413
$R_{w}\left[I > 2.5\sigma(\vec{I})\right]$	0.0440	0.0624
Goodness of fit	1.0332	1.1308

 Table 2
 Comparison of selected bond lengths (Å) in L^{BIS}Cu^{III}OAc and L^{BIS}Cu^{III}CI

L ^{BIS} CuCl		L ^{BIS} CuOAc	
Cu1-N1	1.949(2)	Cu1-N1	1.929(0)
Cu1-N2	1.962(8)	Cu1-N2	1.957(1)
Cu1-O1	2.006(2)	Cu1-O1	1.965(8)
Cu1-Cl1	2.202(2)	Cu1-O101	1.908(8)
C1-C2	1.449(3)	Cu1-C100	2.695(3)
C1-O1	1.273(2)	C22-C23	1.442(3)
C2-C3	1.368(3)	C22-O1	1.275(3)
C3-C4	1.444(3)	C23-C24	1.362(3)
C4-C5	1.361(3)	C24-C25	1.435(3)
C5-C6	1.425(3)	C25-C26	1.359(3)
C1-C6	1.460(3)	C26-C27	1.414(3)
C14-C15	1.396(3)	C22-C27	1.456(3)
C15-C16	1.394(3)	C8-C9	1.386(3)
C16-C17	1.422(3)	C9-C10	1.383(3)
C17-C18	1.388(3)	C10-C11	1.411(3)
C18-C19	1.391(3)	C11-C12	1.384(3)
C14-C19	1.386(3)	C12-C13	1.379(3)
		C8-C13	1.381(3)



Fig. 2 Molecular structure of L^{BIS}Cu^{II}CI. H atoms have been omitted for clarity. Thermal ellipsoids are set at 50% probability.

ion is four-coordinate, bound to the tridentate [LBIS]- ligand, and one chloride ion. The coordination sphere Cu-N distance is 1.949 Å for Cu[1]-N[1] and 1.963 Å for Cu[1]-N[2], comparable with those reported in the literature.^{73,74} The Cu[1]-Cl[1] and Cu[1]–O[1] bonds are 2.202 Å and 2.006 Å respectively. Of immediate interest is the relatively long Cu[1]-O[1] bond. Further analysis of the ring bond lengths for the aminophenolate function allowed for the assignment of the iminosemiquinone redox-state for the [L^{BIS}][–] ligand (Table 2). The relatively short C[2]-C[3] and C[4]-C[5] bond lengths (1.36 Å average) in comparison to the longer C[1]-C[2] and C[5]-C[6] bond lengths (1.44 Å average), and the short C[1]-O[1] bond length (1.273 Å) are further evidence for iminosemiquinone formation. The metrical parameters for LBISCuIICl also match other reports of transition metal iminosemiquinone complexes.75-77

Crystal structure of LBISCuIIOAc

The structure of $L^{BIS}Cu^{II}OAc$ (Fig. 3) is composed of a copper center ligated by the $[L^{BIS}]^-$ ligand and a bidentate acetate molecule. The distortion parameter $\tau = [(\Phi_1 - \Phi_2)/60]$, in which Φ_1 and Φ_2 are the two largest L–M–L angles of the



Fig. 3 Molecular structure of L^{BIS}Cu^{II}OAc. H atoms have been omitted for clarity. Thermal ellipsoids are set at 50% probability.

Cu coordination sphere⁷⁸ for this complex is 0.16. Comparing this τ value with corresponding values for an ideal trigonal bipyramid ($\tau = 1$) and square pyramid ($\tau = 0$) indicates that this complex exhibits a distorted square based pyramidal (SP) structure. In this geometry for L^{BIS}Cu^{II}OAc one nitrogen N[2] of the coordinated benzoxazole ligand, one oxygen atom O[1] and an imine nitrogen N[1] of the iminosemiquinone and the O[101] oxygen atom from the acetate moiety are nearly coplanar, occupying the basal positions of the pyramid whereas the other oxygen atom O[100] occupies the apical position. The observed basal bond lengths (Cu[1]-N[1], 1.929 Å; Cu[1]-N[2], 1.957 Å; Cu[1]-O[101], 1.909 Å; Cu[1]-O[1], 1.966 Å) are in the range of those reported for other square based pyramidal (SP) Cu^{II} complexes containing semiquinone ligands^{79,80} while the apical bond length of Cu[1]-O[100] (2.695 Å) is elongated. The twist in the basal plane (dihedral angle between N[1]-Cu[1]-O[1] and N[2]-Cu[1]-O[101] planes) is 37.7°, which is slightly less in comparison to the LBISCuIICl analogue. The apical oxygen may play a role in reducing the twist in the L^{BIS}Cu^{II}OAc derivative. The relatively short C[23]-C[24] and C[25]-C[26] bond lengths (1.36 Å average) in comparison to the longer C[22]-C[23] and C[26]-C[27] bond lengths (1.43 Å average), and the short C[22]-O[1] bond length (1.275 Å) are further evidence for iminosemiquinone formation.⁷⁵ Overall, the [L^{BIS}]⁻ bond lengths in both the Cu derivatives are very similar. The iminosemiquinone assignment for [L^{BIS}]⁻ results in a possible magnetic interaction with the d⁹ Cu^{II} metal centre.

Magnetic susceptibility measurements

Magnetic susceptibility data for polycrystalline samples of L^{BIS} -Cu^{II}OAc and L^{BIS} Cu^{II}Cl complexes was collected in the temperature range 1.8–290 K with an applied magnetic field of 1000 Oe. The effective magnetic moment per molecule (μ_{eff}) for these complexes remains near zero for all temperatures studied, confirming the diamagnetic nature of the complexes. This observation is consistent with the ¹H NMR characterization; as the spectra of both Cu^{II} complexes contain relatively sharp resonances (ESI Fig. S4 and S5[†]). This result supports the antiferromagnetic coupling between the Cu^{II} and iminosemiquinone ligand radical. The significant twist in the structures (*vide supra*) likely facilitates overlap of the magnetic Cu d_{x²-y²} orbital

with the iminosemiquinone π singly occupied molecular orbital.

Electrochemistry

The electrochemical properties of the HL^{BAP} ligand and its copper complexes were examined by cyclic voltammetry (CV) in CH_2Cl_2 at low temperature (233 K). The ligand HL^{BAP} displays a series of irreversible oxidations (ESI Fig. S6†) under the experimental conditions. In comparison, both Cu complexes exhibit two quasi-reversible one-electron redox processes in the range studied (Fig. 4 and Table 3).

The redox process at negative potentials occurs at essentially the same value for the two Cu complexes (Fig. 4). The $E_{\rm pc}$ – $E_{\rm pa}$ peak separation is slightly larger for the OAc derivative, and could indicate more significant rearrangement for this derivative. This redox process has been assigned as a ligandbased iminosemiquinone/amidophenoxide⁸¹ redox couple on the basis of additional experiments (*vide infra*) (Scheme 3).



Fig. 4 Cyclic voltammograms of $L^{BIS}Cu^{II}OAc$ (black line) and $L^{BIS}Cu^{II}Cl$ (red line). Conditions: 1 mM complex, 0.1 M NBu₄ClO₄, scan rate 100 mV s⁻¹, CH₂Cl₂, 233 K.

Table 3 Redox potentials of $L^{BIS}Cu^{II}OAc$ and $L^{BIS}Cu^{II}CI$ versus Fc^+/Fc^a Peak to peak separation in brackets

Compound	$E_{1/2}^{1}/V$	$E_{1/2}^2/V$
L ^{BIS} Cu ^{II} Cl	-0.57 (0.17)	0.55 (0.16)
L ^{BIS} Cu ^{II} OAc	-0.58 (0.22)	0.28 (0.23)

^{*a*} Peak to peak difference for the Fc⁺/Fc couple at 233 K is 0.080 V.



 $\label{eq:scheme3} \begin{array}{l} \mbox{Scheme3} & \mbox{Schema3} & \mbox{Schem3} & \mbox{Schem3}$



Fig. 5 Electronic spectra of 3 mM CH_2Cl_2 solutions of $L^{BIS}Cu^{II}CI$ (black) and $[L^{BIQ}Cu^{II}CI]^+$ (red) and spectra during incremental oxidation (grey) with $[N(C_6H_3Br_2)_3^-]^+SbF_6^-$ at 195 K.

Interestingly, the redox processes at positive potentials differ by *ca.* 0.27 V for the two Cu complexes, likely due to the different electron-donating effects of Cl⁻ and OAc⁻ anionic ligands. On the basis of EPR experiments (*vide infra*), the couple at positive potentials has been assigned to a ligandbased iminosemiquinone/iminoquinone redox process. Due to the similar properties of L^{BIS}Cu^{II}OAc and L^{BIS}Cu^{II}Cl complexes we chose to perform further experiments on L^{BIS}Cu^{II}Cl.

Electronic spectroscopy

The electronic spectrum of L^{BIS}Cu^{II}Cl in CH₂Cl₂ exhibits a series of bands in the visible region (Fig. 5). An oxidation titration with $[N(C_6H_3Br_2)_3]^+SbF_6^{-82}$ from $0 \rightarrow 1$ equivalent at low temperature (195 K) exhibits an isosbestic point at 26 300 cm⁻¹ upon conversion to the iminoquinone form [L^{BIQ}Cu^{II}Cl]⁺. Upon oxidation, the electronic transitions decrease in intensity in the range studied. In addition, a reduction titration of $\boldsymbol{L}^{\text{BIS}}$ $Cu^{II}Cl$ with cobaltocene from $0 \rightarrow 1$ equivalent at low temperature (195 K) was performed. Due to the limited solubility of cobaltocene in CH2Cl2, a toluene: CH2Cl2 mixture (30:1) was used as the solvent. Slight differences in the intensities of the spectral bands for L^{BIS}Cu^{II}Cl in the two different solvents were evident (Fig. 5 and 6). Upon reduction, isosbestic points at 25 400 and 20 300 cm⁻¹ were observed, as well as a new prominent band at 19 900 cm⁻¹ (Table 4). Samples of both the oxidized and reduced forms of LBISCuIICl prepared by the redox titrations described in this section were transferred to EPR tubes for further analysis.

EPR analysis

A frozen CH₂Cl₂ solution of the neutral species L^{BIS}Cu^{II}Cl is EPR silent at 20 K (Fig. 7b), consistent with a diamagnetic electronic ground state (S = 0) measured in the solid state. In contrast, the reduced complex [L^{BAP}Cu^{II}Cl]⁻ displays a typical pattern for an axially-symmetric d⁹ Cu^{II} complex with $g_1 =$ $g_2 = g_{\perp} = 2.045$ and $g_3 = g_{\parallel} = 2.206$ (Fig. 7c, Table 5). The EPR spectrum of [L^{BAP}Cu^{II}Cl]⁻ provides further evidence that the



Fig. 6 Electronic spectra of 3 mM toluene : CH_2CI_2 (*ca.* 30 : 1) solutions of L^{BIS} -Cu^{II}Cl (black) and $[L^{BAP}Cu^{II}CI]^-$ (red) and spectra during incremental reduction (grey) with cobaltocene at 195 K.

Table 4 Electronic absorption properties of the complexes^a

Complex	$\nu_{\rm max}, {\rm cm}^{-1} \left(\varepsilon_{\rm max}, {\rm M}^{-1} {\rm cm}^{-1} \right)$
L ^{BIS} Cu ^{II} Cl	24 400 (sh, 7300), 23 200 (8800), 20 600 (8100), 16 900
$[L^{BIQ}Cu^{II}Cl]^+$	(5100), 11 300 (2700) 24 400 (sh, 4000), 23 200 (4400), 20 600 (4600), 16 900
[L ^{BAP} Cu ^{II} Cl] ⁻	(2000), 11 300 (1000) 22 600 (8000), 19 900 (12 300), 17 900 (sh, 7900), 15 700
	(sh, 2700), 11 400 (1400)

^a For measurements see Experimental section.

reduction process is ligand-based, likely affording a Cu^{II} amidophenoxide complex.²⁹ The oxidized complex $[L^{BIQ}Cu^{II}Cl]^+$ also displays an EPR signal, but the signal suggests significant distortion from axial symmetry in comparison to the reduced analogue.^{83–86} Fitting the data affords a rhombic spin system with three different *g* values as displayed in Table 5. In addition, the A_3 value is decreased substantially to 330 MHz (*ca.* 118 × 10⁻⁴ cm⁻¹), which suggests significant tetrahedral distortion for this species.^{83–86} We tentatively assign the oxidized species as a distorted Cu^{II} iminoquinone species on the basis of this preliminary analysis. Thus, both redox processes observed for L^{BIS}Cu^{II}Cl are ligand based.

Theoretical analysis

The solid state magnetic data, in combination with the EPR results, demonstrate that the complex $L^{BIS}Cu^{II}Cl$ exhibits a diamagnetic ground state. Thus the complex can be described as one of the following: (i) a d⁸ Cu^{III} amidophenoxide complex, (ii) a Cu^{II} complex antiferromagnetically coupled to an iminosemiquinone ligand radical, or (iii) a Cu^I complex bound to an iminoquinone. The Cu^{II} iminosemiquinone electronic structure is most likely on the basis of the solid state X-ray data. We calculated the relative energies of the triplet and broken symmetry (BS) electronic states for $L^{BIS}Cu^{II}Cl$. BS calculations provide a localized solution for the ground-state wave function.^{62–64,87} The BS solution was determined to be lower

in energy by 1.12 kcal mol⁻¹ in comparison to the triplet, matching the experimental data. The closed-shell singlet solution (S = 0) is found to be higher in energy by 5.49 kcal mol⁻¹ in comparison to the BS solution. The exchange coupling *J* was calculated using the Yamaguchi formula (eqn (1)), which is applicable for systems from the strong to the weak exchange limit.^{88,89} The computed exchange coupling for this complex is -316 cm^{-1} , corresponding to a significant antiferromagnetic (S = 0) exchange interaction for this system. The corresponding orbital transformation (COT) was used to determine the magnetic orbitals for the L^{BIS}Cu^{II}Cl complex.^{90,91} The large distortion in the solid state structure (also predicted by calculations)



Fig. 7 EPR spectrum of (a) oxidized $[L^{BIQ}Cu^{II}CI]^+$ in CH₂CI₂, experimental (black), simulation (red); (b) neutral $L^{BIS}Cu^{II}CI$ in CH₂CI₂, experimental (black); and (c) reduced $[L^{BAP}Cu^{II}CI]^-$ in toluene, experimental (black), simulation (red). Conditions: frequency = (a) 9.381 GHz, (b) 9.381 GHz, (c) 9.381 GHz; power = 2 mW; modulation frequency = 100 kHz; amplitude = 0.6 mT; *T* = 20 K; concentration = 3 mM.

results in substantial overlap between the Cu $d_{x^2-y^2}$ and iminosemiquinone π magnetic orbitals (Fig. 8). The calculated magnetic orbital overlap is 0.49.^{92–94} The computed exchange coupling is likely an underestimation of the singlet–triplet splitting, as no evidence for population of the triplet state was observed in the variable temperature magnetic susceptibility experiment.^{95,96}

$$J = -\frac{E_{\rm HS} - E_{\rm BS}}{\langle \hat{S}^2 \rangle_{\rm HS} - \langle \hat{S}^2 \rangle_{\rm BS}} \tag{1}$$

The optimized geometry (BS solution) is in good agreement with the X-ray data. A comparison of relevant experimental and theoretical bond lengths is shown in Table 6. The iminosemiquinone bonding pattern observed in the X-ray data for $L^{BIS}Cu^{II}Cl$ is predicted by the DFT calculations. This includes the ring bond lengths as well as the relatively short C(1)–O(1) and N(1)–C(6) bonds. The bond lengths are similar to other iminosemiquinone metal complexes reported in the literature.^{76,77} The Cu coordination sphere metrical parameters are also well predicted, a notable exception being a deviation of 0.076 Å between the experimental and calculated Cu(1)–O(1) bond length.

Catalytic activity of L^{BIS}CuX complexes

We were interested in studying the catalytic activity of L^{BIS}-Cu^{II}X for the oxidation of a large number of structurally diverse alcohols to the corresponding aldehydes. Our initial



Fig. 8 Magnetic orbitals for L^{BIS} Cu^{II}Cl showing the Cu d_{x²-y²} and semiquinone π antiferromagnetic interaction.

Table 6 Comparison of experimental and calculated (in parentheses) bond lengths for the $L^{\rm BIS}{\rm Cu}^{\rm II}{\rm Cl}$ complex*

Bond	Bond length (Å)	Bond	Bond length (Å)
$\begin{array}{c} {\rm Cu(1)-O(1)}\\ {\rm Cu(1)-N(1)}\\ {\rm Cu(1)-Cl(1)}\\ {\rm Cu(1)-N(2)}\\ {\rm C(1)-O(1)}\\ {\rm N(1)-C(6)} \end{array}$	2.006 (1.930) 1.949 (1.955) 2.202 (2.214) 1.963 (1.951) 1.273 (1.285) 1.340 (1.355)	C(1)-C(6) C(5)-C(6) C(1)-C(2) C(2)-C(3) C(4)-C(5) C(3)-C(4)	$\begin{array}{c} 1.460 \ (1.464) \\ 1.425 \ (1.420) \\ 1.449 \ (1.442) \\ 1.368 \ (1.378) \\ 1.361 \ (1.379) \\ 1.444 \ (1.436) \end{array}$

^a See Experimental section for calculation details.

Table 5	EPR parameters	for [L ^{BIQ} Cu ^{II} CI] ⁺	and [L ^{BAP} Cu ^{II} CI] ^{-a}
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Compound	g_1	g_2	g_3	A_1^{b} (Cu)	A_2^{b} (Cu)	A_3^{b} (Cu)	$A_{\perp}{}^{b}$ (N)	$A_{\parallel}{}^{b}\left(\mathrm{N} ight)$
[L ^{BAP} Cu ^{II} Cl] ⁻	2.045	2.045	2.206	39	39	499	39	39
[L ^{BIQ} Cu ^{II} Cl] ⁺	2.043	2.118	2.263	103	220	330	—	—

^{*a*} See Experimental section for details. [L^{BAP}Cu^{II}Cl]⁻ in toluene, [L^{BIQ}Cu^{II}Cl]⁺ in CH₂Cl₂. All measurements at 20 K. ^{*b*} Values in MHz.

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Entry		Solvent	L ^{BIS} Cu ^{II} OAc ^a		$L^{BIS}Cu^{II}Cl^b$		
	Base		Time (h)	Conversion (%)	Time (h)	Conversion (%)	
1	4 equiv. K ₃ PO ₄	Toluene	24	31	24	26	
2	4 equiv. K_2CO_3	Toluene	24	19	24	37	
3	4 equiv. Et ₃ N	Toluene	24	7	24	5	
4	1 equiv. Cs_2CO_3	Toluene	24	72	24	63	
5	2 equiv. Cs_2CO_3	Toluene	8	91	4	100	
6	3 equiv. Cs_2CO_3	Toluene	8	94	4	100	

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Table 7 The effect of various bases and solvents for the aerobic oxidation of benzyl alcohol by $L^{BIS}CuX$

CH₃CN

 a 298 K, 4 mmol% $\rm L^{BIS}Cu^{II}OAc.$ b 333 K, 4 mmol% $\rm L^{BIS}Cu^{II}Cl.$

2 equiv. Cs₂CO₃

studies centered on determining the optimal conditions (base and solvent) for the conversion of a representative alcohol (benzyl alcohol) to the corresponding aldehyde. Both L^{BIS} -Cu^{II}Cl and L^{BIS} Cu^{II}OAc were examined under a number of different conditions (Table 7) and it was found that L^{BIS} -Cu^{II}OAc exhibited superior catalytic performance at 298 K. The superior catalytic activity of L^{BIS} Cu^{II}OAc in comparison to L^{BIS} -Cu^{II}Cl could be due to the acetate ligand improving solvation of the complex in toluene, and/or the ability of this ligand to act as a base during catalysis. For all subsequent catalysis studies L^{BIS} Cu^{II}OAc was tested at 298 K, while L^{BIS} Cu^{II}Cl was tested at 333 K. The catalytic studies were completed with one-half the catalyst concentration (on a per Cu basis) in comparison to our recently reported studies on a related dimeric complex.⁷²

It was found that benzyl alcohol conversion was highest when Cs_2CO_3 was used in comparison to other bases (Table 7). For both complexes $L^{BIS}Cu^{II}X$, maximum conversion of benzyl alcohol was achieved with 2 equivalents of Cs_2CO_3 in toluene (Table 7, entries 4–6); but no significant increase was observed when 3 equivalents was used. Toluene was chosen as a solvent based on previous work with similar systems.^{97,98} Changing to the more polar solvent CH_3CN , and utilizing 2 equiv. of Cs_2CO_3 afforded poor results (Table 7, entry 7). Using the optimized conditions (Scheme 4) determined from Table 7 we screened a variety of alcohol substrates as detailed in Table 8.

Under the conditions tested, the alcohols in Table 8 could be oxidized to the corresponding aldehydes with good conversions (>80% entries 1–14). No over-oxidation of the aldehyde to the carboxylic acid was observed by GC analysis. Testing of Cu^{II} salts under our reaction conditions (4 mmol% CuCl₂/2 equiv. Cs₂CO₃ and 4 mmol% Cu(OAc)₂/2 equiv. Cs₂CO₃) demonstrates aldehyde formation, but in comparatively low yield (Table 9). Addition of ligand HL^{BAP} (Table 9, entries 3 and 4) improved the yield in the case of Cu(OAc)₂ but not to the level when preformed L^{BIS}Cu^{II}OAc is used (Table 7, entry 5). These results highlight that the pre-formed complex is necessary to afford high conversion of the tested alcohol substrates.

Conclusion

A new benzoxazole-based aminophenol ligand HL^{BAP} and two corresponding Cu^{II} complexes were synthesized and



2.4

Scheme 4 Catalysis conditions relevant to Table 8.

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characterized. Both metal complexes exhibit an oxidized iminosemiquinone chelated to the metal ion to afford L^{BIS-}Cu^{II}OAc and L^{BIS}Cu^{II}Cl, which were characterized by a variety of methods. X-ray crystallography revealed that the bond lengths are consistent with a Cu^{II} centre and an iminosemiquinone ligand. The isolation of a Cu^{II} complex containing a tridentate redox active ligand that can be both oxidized and reduced, and in addition, an exchangeable co-ligand, provided an interesting platform for reactivity studies.

Variable temperature magnetic susceptibility measurements in combination with ¹H NMR demonstrated both complexes are diamagnetic due to strong antiferromagnetic coupling between the Cu dx2-y2 orbital and the iminosemiquinone π singly occupied molecular orbital. EPR studies on the $L^{BIS}Cu^{II}Cl$ analogue were in agreement with an S =0 ground state. Theoretical calculations on this complex also predict that the antiferromagnetically coupled electronic state is lowest in energy, with a computed exchange coupling of -316 cm⁻¹. Cyclic voltammetry measurements showed two quasi-reversible redox events for both Cu complexes, suggesting that the L^{BIS}Cu^{II}X complexes can be both oxidized and reduced. Chemical redox titrations and EPR analysis of the reduced [L^{BAP}Cu^{II}Cl]⁻ and oxidized [L^{BIQ}Cu^{II}Cl]⁺ species suggested that the redox events are ligand-based. Preliminary reactivity studies show that both Cu complexes particularly the acetate complex are competent catalysts for the oxidation of alcohols in the presence of O2. Based on our results, both complexes are capable of catalyzing the oxidation of a large number of alcohols to the corresponding aldehyde. Of note, the acetate complex generally performed better than the chloride analog. It may be possible to improve the catalytic activity of these complexes through modifications to the ligand framework to fine tune the electronics around the metal center. This

Table 8 L^{BIS}Cu^{II}X-catalyzed aerobic oxidation of different alcohols

		L ^{BIS} Cu	^{II} OAc ^{<i>a</i>}	$L^{BIS}Cu^{II}Cl^b$		
Entry	Substrate	Time (h)	Conversion (%)	Time (h)	Conversion (%)	
1	ОН	8	91	4	94	
2	ОН	6	94	24	60	
3	OH	6	81	6	85	
4	ОН	8	70	8	96	
5	СІОН	6	95	6	81	
6	OH	6	98	6	83	
7)(_)-OH	10	83	8	80	
8	Br	6	90	6	94	
9	сіСіОН	8	97	10	87	
10	СІОН	10	94	6	84	
11	OH NO2	24	71	6	99	
12	O ₂ N OH	8	95	_	_	
13	MeS	36	87	_	_	
14	n-C ₈ H ₁₇ OH	8	98	8	96	
a 200 K	4 mmol% I BISCI	^{II}OAc b	22 K 4 mmol	L BISCUI		

" 298 K, 4 mmol% L^{ыз}Cu^пOAc. ^{*v*} 333 K, 4 mmol% L^{ыз}Cu^пOCl.

 Table 9
 Blank tests with HL^{BAP} and copper salts^a

Entry	Catalytic system	Temp. (K)	Solvent	Time (h)	Conversion (%)
1	CuCl ₂ /Cs ₂ CO ₂	333	Toluene	24	28
2	$Cu(OAc)_2/Cs_2CO_3$	298	Toluene	24	24
3	CuCl ₂ /Cs ₂ CO ₃ /HL ^{BAP}	333	Toluene	8	8
4	$Cu(OAc)_2/Cs_2CO_3/$ HL ^{BAP}	298	Toluene	8	50
5	$\mathrm{HL}^{\mathrm{BAP}}\!/\mathrm{Cs}_{2}\mathrm{CO}_{3}$	298	Toluene	8	5

 $[^]a$ Reaction conditions: 4 mmol% CuCl_2/Cu(OAc)_2/HL BAP and 2 equiv. Cs2CO3.

will be particularly important for the future development of bioinspired catalysts.

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References

- 1 J. Stubbe and W. A. van der Donk, *Chem. Rev.*, 1998, 98, 705–762.
- 2 J. W. Whittaker, Chem. Rev., 2003, 103, 2347-2364.
- 3 K. J. Blackmore, N. Lal, J. W. Ziller and A. F. Heyduk, *J. Am. Chem. Soc.*, 2008, **130**, 2728–2729.
- 4 T. Büttner, J. Geier, G. Frison, J. Harmer, C. Calle, A. Schweiger, H. Schönberg and H. Grützmacher, *Science*, 2005, **307**, 235–238.
- 5 P. J. Chirik, Inorg. Chem., 2011, 50, 9737-9740.
- 6 P. J. Chirik and K. Wieghardt, Science, 2010, 327, 794-795.
- 7 M. R. Haneline and A. F. Heyduk, J. Am. Chem. Soc., 2006, 128, 8410–8411.
- 8 C. C. Hojilla Atienza, C. Milsmann, E. Lobkovsky and P. J. Chirik, *Angew. Chem., Int. Ed.*, 2011, **50**, 8143–8147.
- 9 M. Königsmann, N. Donati, D. Stein, H. Schönberg, J. Harmer, A. Sreekanth and H. Grützmacher, *Angew. Chem., Int. Ed.*, 2007, 46, 3567–3570.
- 10 P. Maire, M. Königsmann, A. Sreekanth, J. Harmer, A. Schweiger and H. Grützmacher, *J. Am. Chem. Soc.*, 2006, 128, 6578–6580.
- 11 W. R. McNamara, Z. Han, P. J. Alperin, W. W. Brennessel, P. L. Holland and R. Eisenberg, *J. Am. Chem. Soc.*, 2011, 133, 15368–15371.
- 12 Y. Miyazato, T. Wada and K. Tanaka, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 745–747.
- 13 M. R. Ringenberg, S. L. Kokatam, Z. M. Heiden and T. B. Rauchfuss, J. Am. Chem. Soc., 2008, 130, 788–789.
- 14 S. K. Russell, E. Lobkovsky and P. J. Chirik, J. Am. Chem. Soc., 2011, 133, 8858–8861.
- 15 L. Benisvy, A. J. Blake, D. Collison, E. S. Davies, C. D. Garner, E. J. L. McInnes, J. McMaster, G. Whittaker and C. Wilson, *Chem. Commun.*, 2001, 1824–1825.
- 16 P. Chaudhuri, M. Hess, U. Flörke and K. Wieghardt, Angew. Chem., Int. Ed., 1998, 37, 2217–2220.
- P. Chaudhuri, M. Hess, J. Müller, K. Hildenbrand, E. Bill, T. Weyhermüller and K. Wieghardt, *J. Am. Chem. Soc.*, 1999, 121, 9599–9610.
- 18 J. A. Halfen, B. A. Jazdzewski, S. Mahapatra, L. M. Berreau, E. C. Wilkinson, L. Que and W. B. Tolman, *J. Am. Chem. Soc.*, 1997, **119**, 8217–8227.
- 19 F. Michel, F. Thomas, S. Hamman, C. Philouze, E. Saint-Aman and J.-L. Pierre, *Eur. J. Inorg. Chem.*, 2006, 3684–3696.
- 20 R. C. Pratt and T. D. P. Stack, J. Am. Chem. Soc., 2003, 125, 8716-8717.
- 21 R. C. Pratt and T. D. P. Stack, *Inorg. Chem.*, 2005, 44, 2367–2375.
- 22 B. A. Jazdzewski and W. B. Tolman, *Coord. Chem. Rev.*, 2000, **200–202**, 633–685.

- 23 A. Ghosh, T. Wondimagegn and A. B. J. Parusel, *J. Am. Chem. Soc.*, 2000, **122**, 5100–5104.
- 24 W. Kaim, M. Wanner, A. Knödler and S. Záliš, *Inorg. Chim. Acta*, 2002, **337**, 163–172.
- 25 V. Kasack, W. Kaim, H. Binder, J. Jordanov and E. Roth, *Inorg. Chem.*, 1995, **34**, 1924–1933.
- 26 P. Chaudhuri, R. Wagner, U. Pieper, B. Biswas and T. Weyhermuller, *Dalton Trans.*, 2008, 1286–1288.
- 27 R. Hübner, B. Sarkar, J. Fiedler, S. Záliš and W. Kaim, *Eur. J. Inorg. Chem.*, 2012, 3569–3576.
- 28 K. S. Min, T. Weyhermüller, E. Bothe and K. Wieghardt, *Inorg. Chem.*, 2004, 43, 2922–2931.
- 29 C. Mukherjee, U. Pieper, E. Bothe, V. Bachler, E. Bill, T. Weyhermüller and P. Chaudhuri, *Inorg. Chem.*, 2008, 47, 8943–8956.
- 30 C. Nazari Verani, S. Gallert, E. Bill, T. Weyhermuller, K. Wieghardt and P. Chaudhuri, *Chem. Commun.*, 1999, 1747–1748.
- 31 A. V. Piskunov, I. N. Meshcheryakova, E. V. Baranov, G. K. Fukin, V. K. Cherkasov and G. A. Abakumov, *Russ. Chem. Bull.*, 2010, **59**, 361–370.
- 32 V. Bachler, P. Chaudhuri and K. Wieghardt, *Chem.-Eur. J.*, 2001, 7, 404–415.
- 33 P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller and K. Wieghardt, *J. Am. Chem. Soc.*, 2001, 123, 2213–2223.
- 34 G. Speier, J. Csihony, A. M. Whalen and C. G. Pierpont, *Inorg. Chem.*, 1996, 35, 3519–3524.
- 35 A. R. Silva, H. Albuquerque, S. Borges, R. Siegel, L. Mafra,
 A. P. Carvalho and J. Pires, *Microporous Mesoporous Mater.*,
 2012, 158, 26–38.
- 36 J.-H. Chen, S.-H. Liao, X.-L. Sun, Q. Shen and Y. Tang, *Tetrahedron*, 2012, 68, 5042–5045.
- 37 A. Bisai and V. K. Singh, Tetrahedron, 2012, 68, 3480-3486.
- 38 W. Yang and D.-M. Du, Eur. J. Org. Chem., 2011, 1552–1556.
- 39 L. Wen, Q. Shen, X. Wan and L. Lu, J. Org. Chem., 2011, 76, 2282–2285.
- 40 A. R. Silva, H. Albuquerque, A. Fontes, S. Borges, Â. Martins, A. P. Carvalho and J. Pires, *Ind. Eng. Chem. Res.*, 2011, 50, 11495–11501.
- 41 M. Rostami, A. Khosropour, V. Mirkhani, M. Moghadam, S. Tangestaninejad and I. Mohammadpoor-Baltork, *Appl. Catal.*, A, 2011, 397, 27–34.
- 42 Y. Motoyama, T. Nishikata and H. Nagashima, *Chem.–Asian J.*, 2011, **6**, 78–82.
- 43 D. Didier, C. Magnier-Bouvier and E. Schulz, *Adv. Synth. Catal.*, 2011, 353, 1087–1095.
- 44 F. Riobé and N. Avarvari, *Coord. Chem. Rev.*, 2010, 254, 1523–1533.
- 45 J.-M. Lee, J. Kim, Y. Shin, C.-E. Yeom, J. E. Lee, T. Hyeon and B. Moon Kim, *Tetrahedron: Asymmetry*, 2010, 21, 285–291.
- 46 K. Lang, J. Park and S. Hong, J. Org. Chem., 2010, 75, 6424-6435.
- 47 G. Chollet, D. Didier and E. Schulz, *Catal. Commun.*, 2010, 11, 351–355.

- 48 P. Cao, C. Deng, Y. Y. Zhou, X. L. Sun, J. C. Zheng, Z. Xie and Y. Tang, Angew. Chem., Int. Ed., 2010, 49, 4463–4466.
- 49 Y.-J. Sun, N. Li, Z.-B. Zheng, L. Liu, Y.-B. Yu, Z.-H. Qin and B. Fu, *Adv. Synth. Catal.*, 2009, **351**, 3113–3117.
- 50 M. Schönleber, R. Hilgraf and A. Pfaltz, *Adv. Synth. Catal.*, 2008, **350**, 2033–2038.
- 51 R. Rasappan, D. Laventine and O. Reiser, *Coord. Chem. Rev.*, 2008, 252, 702–714.
- 52 H.-M. Li, J.-G. Su, Z.-L. Lu, H.-K. Fun and S. Chantrapromma, *Inorg. Chem. Commun.*, 2008, **11**, 235–238.
- 53 M. Gómez, G. Muller and M. Rocamora, *Coord. Chem. Rev.*, 1999, **193–195**, 769–835.
- 54 O. Iasco, G. Novitchi, E. Jeanneau, J. B. Tommasino, N. Roques and D. Luneau, *Inorg. Chem.*, 2012, 51, 2588–2596.
- 55 C. J. Richards and A. J. Locke, *Tetrahedron: Asymmetry*, 1998, 9, 2377–2407.
- 56 A. Togni and L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, 1994, 33, 497–526.
- 57 T. Khomenko, O. Salomatina, S. Kurbakova, I. Il'ina, K. Volcho, N. Komarova, D. Korchagina, N. Salakhutdinov and A. Tolstikov, *Russ. J. Org. Chem.*, 2006, 42, 1653–1661.
- 58 S. Stoll and A. Schweiger, J. Magn. Reson., 2006, 178, 42–55.
- 59 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, Bakken, C. Adamo, J. Jaramillo, R. Gomperts, V. R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. К. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, Al-Laham, C. Y. Peng, A. Nanayakkara, M. Α. M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT, 2009.
- 60 A. D. Becke, J. Chem. Phys., 1993, 98, 5648.
- 61 P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, J. Phys. Chem., 1994, 98, 11623–11627.
- 62 L. Noodleman, J. Chem. Phys., 1981, 74, 5737-5743.
- 63 L. Noodleman and D. A. Case, *Adv. Inorg. Chem.*, 1992, 38, 423.
- 64 L. Noodleman and E. R. Davidson, *Chem. Phys.*, 1986, **109**, 131–143.
- 65 A. Schafer, H. Horn and R. Ahlrichs, J. Chem. Phys., 1992, 97, 2571–2577.

- 66 A. Schafer, C. Huber and R. Ahlrichs, J. Chem. Phys., 1994, 100, 5829–5835.
- 67 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343–350.
- 68 P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Crystallogr.*, 2003, **36**, 1487–1487.
- 69 L. Farrugia, J. Appl. Crystallogr., 1997, 30, 565.
- 70 *Persistence of VisionTM Raytracer*, Persistence of Vision Pty. Ltd., Williamstown, Victoria, Australia, 2004.
- 71 The X-ray data for HL^{BAP} could not be fully solved. Selected data: empirical formula, C_{70.5}H₉₃N₄O₄Cl; formula weight, 569.22; crystal system, triclinic; space group, *P*Ī; *a*(Å), 14.2265(6); *b*(Å), 16.3701(7); *c*(Å), 16.7959(8); *α* (°), 74.1570 (10); *β* (°), 88.5650(10); *γ* (°), 65.7200(10); *V* (Å³), 3413.1(3); *Z*, 1; *T* (K), 298.
- 72 S. E. Balaghi, E. Safaei, M. Rafiee and M. H. Kowsari, *Polyhedron*, 2012, 47, 94–103.
- 73 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, 5, 143–207.
- 74 R. W. Saalfrank, M. Decker, F. Hampel, K. Peters and H. G. von Schnering, *Chem. Ber.*, 1997, **130**, 1309–1313.
- 75 S. N. Brown, Inorg. Chem., 2012, 51, 1251-1260.
- 76 A. V. Piskunov, I. N. Mescheryakova, G. K. Fukin,
 V. K. Cherkasov and G. A. Abakumov, *New J. Chem.*, 2010,
 34, 1746–1750.
- 77 A. M. Reynolds, E. A. Lewis, N. W. Aboelella and W. B. Tolman, *Chem. Commun.*, 2005, 2014–2016.
- 78 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, J. Chem. Soc., Dalton Trans., 1984, 1349–1356.
- 79 P. J. Alonso, M. Fraile, I. Garcı and C. Sa, *Langmuir*, 2000, 16, 5607–5612.
- 80 G. Desimoni, G. Faita, M. Toscanini and M. Boiocchi, *Chem.-Eur. J.*, 2009, **15**, 9674-9677.
- 81 A. I. Poddel'sky, V. K. Cherkasov and G. a. Abakumov, *Coord. Chem. Rev.*, 2009, 253, 291–324.
- 82 A. Bjorn, A Mechanistic Investigation of the Photochemical and Thermal Activation of 2,2- and 2,3-Diaryl and 2,2,3-Triaryl-2,3-dihydro-phenanthro[9,10-b]-1,4-dioxins, a New

Class of 1,4-Dioxene Based DNA Cleaving Agents, University of Cincinnati, Cincinnati, 2002.

- 83 F. G. Herring, D. J. Patmore and A. Storr, J. Chem. Soc., Dalton Trans., 1975, 711–717.
- 84 A. A. Gewirth, S. L. Cohen, H. J. Schugar and E. I. Solomon, *Inorg. Chem.*, 1987, 26, 1133–1146.
- 85 S.-k. Kang, H.-s. Kim and Y.-i. Kim, Bull. Korean Chem. Soc., 2004, 25, 1959–1962.
- 86 S. Ghosh, J. Cirera, M. A. Vance, T. Ono, K. Fujisawa and E. I. Solomon, *J. Am. Chem. Soc.*, 2008, **130**, 16262–16273.
- 87 J. Li, L. Noodleman and D. A. Case, in *Inorganic Electronic Structure and Spectroscopy*, ed. E. I. Solomon and A. B. P. Lever, John Wiley & Sons, New York, 1999, vol. I, pp. 661–724.
- 88 T. Soda, Y. Kitagawa, T. Onishi, Y. Takano, Y. Shigeta, H. Nagao, Y. Yoshioka and K. Yamaguchi, *Chem. Phys. Lett.*, 2000, **319**, 223–230.
- 89 K. Yamaguchi, Y. Takahara and T. Fueno, in *Applied Quantum Chemistry*, ed. V. H. Smith, Reidel, Dordrecht, 1986.
- 90 D. Herebian, K. E. Wieghardt and F. Neese, J. Am. Chem. Soc., 2003, 125, 10997–11005.
- 91 F. Neese, J. Phys. Chem. Solids, 2004, 65, 781-785.
- 92 S. Gorelsky and E. Solomon, Theor. Chem. Acc., 2007, 119, 57–65.
- 93 S. I. Gorelsky, AOMix: Program for Molecular Orbital Analysis, http://www.sg-chem.net/, University of Ottawa, Canada, 2007.
- 94 S. I. Gorelsky and A. B. P. Lever, J. Organomet. Chem., 2001, 635, 187–196.
- 95 L. K. Thompson, F. W. Hartstock, P. Robichaud and W. Hanson, *Can. J. Chem.*, 1984, 62, 2755–2762.
- 96 A. Yatani, M. Fujii, Y. Nakao, S. Kashino, M. Kinoshita, W. Mori and S. Suzuki, *Inorg. Chim. Acta*, 2001, 316, 127–131.
- 97 J. M. Hoover and S. S. Stahl, J. Am. Chem. Soc., 2011, 133, 16901–16910.
- 98 L. Liang, G. Rao, H.-L. Sun and J.-L. Zhang, Adv. Synth. Catal., 2010, 352, 2371–2377.