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# Flexible SNS pincer complexes of copper: synthesis, structural characterisation and application in *n*-octane oxidation

Lynette Soobramoney<sup>[a]</sup>, Muhammad D. Bala<sup>\*[a]</sup>, Holger B. Friedrich<sup>[a]</sup> and Michael N. Pillay<sup>[a]</sup>

**Abstract:** Two new tridentate SNS ligands based on a flexible, straight chain amine backbone were prepared and in combination with three related but previously reported ligands were reacted with CuCl<sub>2</sub> to yield new tridentate pincer-type copper(II) complexes. The molecular structures of the new ligands bis(cyclohexylthioethyl)methylamine (**L1d**), bis(*t*butylthioethyl)methylamine (**L1e**), and all the complexes Cu[bis(Rthioethyl)methylamine]Cl<sub>2</sub> (**1**) where R = methyl (**a**); ethyl (**b**); butyl (**c**); cyclohexyl (**d**) and *t*-butyl (**e**); were confirmed by a range of spectroscopic and analytical techniques. Single crystal X-ray diffraction analysis determined the solid-state structures of the salt of **L1e** and the complexes. Complexes **1a-e** all exhibited five-coordinate ligand geometry around each Cu(II) centre defined by the tridentate SNS and two chlorido donors. The complexes were applied as catalysts in the oxidation of *n*octane using *t*-butyl hydroperoxide and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as oxidants. The H<sub>2</sub>O<sub>2</sub> based systems yielded up to 36% conversion of *n*-octane to C-8 oxygenates with very high alcohol selectivity of up to 78%.

Keywords: Pincer ligands; SNS donors; Copper catalysis, Octane oxidation.

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#### 1. Introduction

Pincer complexes containing SNS ligand frameworks have received relatively less attention in comparison to other pincers like the popular PNP donor set. However, since the discovery of SNS complexes of chromium<sup>1-6</sup> as useful ethylene trimerisation catalysts, research exploring the SNS pincer backbone has advanced. To date, SNS pincer complexes of Cr(III),<sup>1</sup> Mo(III),<sup>7</sup> W(IV),<sup>8</sup> Ru(II),<sup>9-11</sup> Co(II),<sup>12</sup> Ir(I),<sup>13</sup> Ni(II),<sup>14</sup> Pd(II),<sup>15,16</sup> Pt(II),<sup>17,18</sup> Cu(II),<sup>19</sup> Zn(II),<sup>20-22</sup> Cd(II),<sup>23</sup> and Hg(II)<sup>23</sup> have been successfully synthesised and characterised. The synthesis of these compounds is generally straightforward and does not usually involve rigorous inert conditions as required for air sensitive phosphine-based tridentate ligands. Another added advantage of the tridentate SNS donor set is the mixed donor strength (soft S- and hard N-donors) of the backbone, which renders the ligands hemilabile, an attractive feature that may be exploited in catalytic applications of resulting complexes.

There are many reports on the application of copper(II) complexes containing SNS ligands as catalysts in cycloaddition reactions<sup>19,24</sup> as well as in the polymerisation of methyl methacrylate.<sup>25,26</sup> In an earlier study,<sup>12</sup> we reported on cobalt(II) complexes containing pincer-type SNS ligands with a linear straight chain amine and a constrained six-membered pyridine ring as the N-donors of the ligands. In that study, the flexibility of the ligand backbone was observed to be the key driver of catalyst activity such that the amine-based complexes proved to be the more efficient catalysts with significantly higher substrate conversions when compared to the more rigid pyridine-based variants. However, due to the unconstrained geometric disposition of the elements around the pincer backbone, the amine-based SNS ligands also yielded complexes that were unstable and challenging to handle.

Hence, in this study, we present a series of SNS pincer complexes of copper(II) with a modified amine N-donor backbone, aimed at circumventing the instability concerns of the previous Co(II) series of complexes combined with the well-established catalytic abilities of Cu<sup>2+</sup> ions in oxidation reactions.<sup>27-30</sup> Therefore, we herein present an exploration on the relationship between ligand backbone flexibility and catalytic activity of Cu(II) complexes containing pincer SNS ligands.

#### 2. Experimental Section

#### 2.1 General

An inert nitrogen atmosphere was employed for the synthesis of the ligands and complexes. All solvents were dried according to standard methods<sup>31</sup> and dissolved oxygen was purged with high purity nitrogen gas prior to use. Diethyl ether (Et<sub>2</sub>O) and tetrahydrofuran (THF) were dried over sodium wire and benzophenone, absolute ethanol (EtOH) and methanol (MeOH) were dried over magnesium turnings and iodine, and dichloromethane (DCM) was dried over phosphorous pentoxide. All other reagents were purchased commercially and used as received. All NMR spectra were recorded using a Bruker Avance<sup>III</sup> 400 MHz spectrometer at ambient temperature. The <sup>1</sup>H NMR data are reported as chemical shift ( $\delta$ , ppm) and referenced to the solvent peak CDCl<sub>3</sub>. The proton decoupled <sup>13</sup>C NMR data are presented as chemical shift ( $\delta$ , ppm) and referenced to the solvent peak CDCl<sub>3</sub> with the specific carbon indicated in parentheses. The <sup>13</sup>C APT NMR data, which distinguishes between quaternary C, CH, CH<sub>2</sub> and CH<sub>3</sub> carbons, are listed as chemical shift ( $\delta$ , ppm) and positive (pos) or negative (neg) with the corresponding carbons in parentheses. The IR spectra were recorded on a Perkin Elmer attenuated total reflectance (ATR) spectrophotometer and elemental analyses were performed on a Thermo-Scientific Flash 2000 CHNS/O elemental analyzer, the HRMS was recorded on a Waters Micromass LCT Premier TOF-MS, while the melting points were determined using a Stuart Scientific melting point apparatus. Recently, we communicated the synthetic procedures and full characterisation of ligands L1a-c (Scheme 1).<sup>32</sup>

#### 2.1.1 Synthesis and characterisation of new ligands and complexes

**bis**(**Cyclohexylthioethyl**)**methylamine** (**L1d**). This ligand was synthesized according to a procedure we previously reported,<sup>32</sup> with the following masses and volumes: 3.454 g (22.1 mmol) of bis(2-chloroethyl)methylamine, 1.527 g (66.4 mmol) of sodium metal and 8.1 ml (66.4 mmol) of cyclohexanethiol. The cream residue obtained after evacuation of the solvent was purified on a silica column, first with hexane to remove excess starting material and then with

5% MeOH in DCM to elute the product, which was isolated as a pale yellow oil. Yield: 84%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.19-1.31 (m, 12H, C<sub>6</sub>H<sub>12</sub>-S), 1.73 (m, 4H, C<sub>6</sub>H<sub>12</sub>-S), 1.93 (m, 4H, C<sub>6</sub>H<sub>12</sub>-S), 2.25 (s, 3H, CH<sub>3</sub>-N), 2.55-2.63 (m, 10H, C<sub>6</sub>H<sub>12</sub>-S, CH<sub>2</sub>CH<sub>2</sub>-N). <sup>13</sup>C APT NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  25.83 (C<sub>6</sub>H<sub>12</sub>-S) pos, 26.09 (C<sub>6</sub>H<sub>12</sub>-S) pos, 27.68 (CH<sub>2</sub>CH<sub>2</sub>-N) pos, 33.78 (C<sub>6</sub>H<sub>12</sub>-S) pos, 42.09 (C<sub>6</sub>H<sub>12</sub>-S) neg, 43.72 (CH<sub>3</sub>-N) neg, 57.76 (CH<sub>2</sub>CH<sub>2</sub>-N) pos. HRMS ESI (*m*/*z*) Calcd for: C<sub>17</sub>H<sub>33</sub>NS<sub>2</sub>Na = 338.1952. Found: 338.1949. IR v<sub>max</sub> (cm<sup>-1</sup>): 2924 (s), 2850 (m), 2788 (w), 1447 (s), 999 (m), 745 (w).

**bis**(*t*-**Butylthioethyl)methylamine** (**L1e**). This ligand was synthesized and purified similarly following our method,<sup>32</sup> with the following masses and volumes: 1.163 g (7.5 mmol) of bis(2-chloroethyl)methylamine, 0.539 g (23.4 mmol) of sodium metal and 2.6 ml (23.4 mmol) of *tert*-butylthiol. The product was isolated as an orange oil. Yield: 80%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.33 (s, 18H, C<sub>4</sub>H<sub>9</sub>-S), 2.32 (s, 3H, CH<sub>3</sub>-N), 2.63 (m, 8H, CH<sub>2</sub>CH<sub>2</sub>-N). <sup>13</sup>C APT NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  26.00 (CH<sub>2</sub>CH<sub>2</sub>-N) pos, 31.01 (C<sub>4</sub>H<sub>9</sub>-S) neg, 41.97 (C<sub>4</sub>H<sub>9</sub>-S) pos, 42.07 (CH<sub>3</sub>-N) neg, 57.53 (CH<sub>2</sub>CH<sub>2</sub>-N) pos. HRMS ESI (*m*/*z*) Calcd for: C<sub>13</sub>H<sub>29</sub>NS<sub>2</sub>Na = 286.1639. Found: 286.1637. IR v<sub>max</sub> (cm<sup>-1</sup>): 2959 (s), 2899 (w), 2862 (w), 2790 (w), 1458 (s), 1363 (s), 1162 (s), 1055 (m), 750 (w).

**Cu[bis(methylthioethyl)methylamine] (1a).** A solution of **L1a** (0.1759 g, 0.98 mmol) in 4 ml of MeOH was added to a light green MeOH solution (4 ml) of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.1672 g, 0.98 mmol). Immediately, a colour change from light to dark green was observed and a green precipitate began to form. The reaction mixture was allowed to stir at room temperature for 2 h, after which the volume was reduced to ~2 ml and filtered via cannula. The precipitate was washed several times with 3 ml portions of Et<sub>2</sub>O and dried to yield a green microcrystalline solid. Single crystals suitable for X-ray diffraction were grown from the mother liquor. Yield: 71%. Melting point: 133-134 °C. HRMS ESI (*m*/*z*) Calcd for: C<sub>7</sub>H<sub>17</sub>NS<sub>2</sub>Cu = 242.0098. Found = 242.0094. IR  $v_{max}$  (cm<sup>-1</sup>): 2991 (w), 2963 (w), 2916 (m), 2857 (w), 2808 (w), 1472 (m), 1441 (s), 1424 (s), 1231 (m), 1085 (m), 741 (s). Anal. (%) calc. for C<sub>7</sub>H<sub>17</sub>NS<sub>2</sub>CuCl<sub>2</sub>: C, 26.8; H, 5.5; N, 4.5; found: C, 26.8; H, 5.6; N, 4.5.

Cu[bis(ethylthioethyl)methylamine] (1b). This complex was synthesized analogously to 1a with the following masses: 0.142 g (0.69 mmol) of L1b and 0.1167 g (0.69 mmol) of CuCl<sub>2</sub>·2H<sub>2</sub>O. A colour change from light to dark green was observed, however no precipitate had

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formed, and therefore the reaction was left to stir overnight at room temperature. The solution was concentrated and a green oil crashed out upon the addition of Et<sub>2</sub>O. After decanting the solvent, the oil was extracted with DCM and hexane. Upon evacuation of the supernatant, a dark green crystalline solid was obtained. Single crystals suitable for analysis were grown by slow diffusion of Et<sub>2</sub>O into a concentrated MeOH solution of **1b**. Yield: 64%. Melting point: 118-119 °C. HRMS ESI (*m*/*z*) Calcd for: C<sub>9</sub>H<sub>21</sub>NS<sub>2</sub>Cu = 270.0411. Found = 269.9984. IR v<sub>max</sub> (cm<sup>-1</sup>): 2961 (w), 2924 (w), 2866 (m), 1472 (w), 1446 (s), 1423 (m), 1380 (m), 1231 (m), 1086 (m), 735 (s). Anal. (%) calc. for C<sub>9</sub>H<sub>21</sub>NS<sub>2</sub>CuCl<sub>2</sub>: C, 31.6; H, 6.2; N, 4.1; found: C, 31.6; H, 6.3; N, 4.1.

**Cu[bis(butylthioethyl)methylamine] (1c).** A similar procedure as **1b** was followed to obtain **1c** with the following masses: 0.232 g (0.88 mmol) of **L1c** and 0.147 g (0.86 mmol) of CuCl<sub>2</sub>·2H<sub>2</sub>O. An analogous colour change as the previous reactions was observed and the reaction solution was evacuated to dryness after stirring overnight. The green residue was washed with Et<sub>2</sub>O, taken up in 3 ml of DCM and the product crashed out as a green powder upon the addition of 2 ml of Et<sub>2</sub>O. The filtrate was removed by cannula and the solid was washed several times with Et<sub>2</sub>O and dried under vacuum to afford a bright green powder. Single crystals suitable for analysis were grown from a solution of **1c** in DCM layered with Et<sub>2</sub>O. Yield: 81%. Melting point: 101-103 °C. HRMS ESI (*m/z*) Calcd for: C<sub>13</sub>H<sub>29</sub>NS<sub>2</sub>Cu = 326.1037. Found = 326.0524. IR  $v_{max}$  (cm<sup>-1</sup>): 2958 (w), 2930 (m), 2871 (m), 1463 (s), 1426 (m), 1224 (m), 1043 (m), 736 (s). Anal. (%) calc. for C<sub>13</sub>H<sub>29</sub>NS<sub>2</sub>CuCl<sub>2</sub>: C, 39.2; H, 7.4; N, 3.5; found: C, 39.2; H, 7.6; N, 3.6.

Cu[bis(cyclohexylthioethyl)methylamine] (1d). A similar procedure as complex 1b was adapted to synthesize complex 1d with the following masses: 0.210 g (0.67 mmol) of L1d and 0.112 g (0.66 mmol) of CuCl<sub>2</sub>·2H<sub>2</sub>O. The solution was concentrated to 1 ml and stirred in 10 ml of Et<sub>2</sub>O overnight. A dark green solid was obtained, which was washed with several portions of Et<sub>2</sub>O and dried *in vacuo*. Single crystals were grown from a MeOH solution layered with heptane. Yield: 92%. Melting point: 120-121 °C. HRMS ESI (*m*/*z*) Calcd for: C<sub>17</sub>H<sub>33</sub>NS<sub>2</sub>Cu = 378.1350.

Found = 378.0914. IR  $\nu_{max}$  (cm<sup>-1</sup>): 2922 (s), 2850 (m), 1447 (s), 1265 (m), 1042 (w), 732 (m). Anal. (%) calc. for C<sub>17</sub>H<sub>33</sub>NS<sub>2</sub>CuCl<sub>2</sub>: C, 45.4; H, 7.4; N, 3.1; found: C, 45.4; H, 7.3; N, 2.8.

**Cu[bis(***t***-butylthioethyl)methylamine] (1e).** A similar procedure as **1a** was adapted to synthesize **1e** with the following masses: 0.140 g (0.53 mmol) of **L1e** and 0.090 g (0.53 mmol)

of CuCl<sub>2</sub>·2H<sub>2</sub>O. A precipitate formed within a few minutes, however the reaction mixture was allowed to stir at room temperature for a further 2 h, after which the mixture was concentrated to ~3 ml and filtered via cannula. The precipitate was washed several times with 3 ml portions of Et<sub>2</sub>O and dried to yield a lime green powder. Single crystals suitable for X-ray diffraction were grown from a DCM solution of **1e** layered with Et<sub>2</sub>O. Yield: 73%. Melting point: 118-119 °C. HRMS ESI (*m/z*) Calcd for:  $C_{13}H_{29}NS_2Cu = 326.1037$ . Found = 326.1037. IR  $v_{max}$  (cm<sup>-1</sup>): 2956 (w), 2862 (m), 1461 (m), 1363 (m), 1209 (m), 1163 (s), 998 (m), 745 (m). Anal. (%) calc. for  $C_{13}H_{29}NS_2CuCl_2$ : C, 39.2; H, 7.4; N, 3.5; found: C, 39.0; H, 7.3; N, 3.2.

#### 2.1.2 Crystallographic analyses

Single-crystal X-ray diffraction data were collected on a Bruker KAPPA APEX II DUO diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\chi = 0.71073$  Å). Data collection was carried out at 296(2), 173(2) or 100(2) K. Temperature was controlled by an Oxford Cryostream cooling system (Oxford Cryostat). Cell refinement and data reduction were performed using the program SAINT.<sup>33</sup> The data were scaled and absorption correction performed using SADABS.<sup>34</sup> The structure was solved by direct methods using SHELXS<sup>34</sup> and refined by full-matrix least-squares methods based on  $F^2$  using SHELXL<sup>34</sup> and using the graphics interface program X-Seed<sup>35,36</sup>. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in idealised positions and refined in riding models with U<sub>iso</sub> assigned 1.2 or 1.5 times U<sub>eq</sub> of their parent atoms with C-H bond distances constrained to 0.98 or 0.99 Å. Molecular structures and packing diagrams were generated using the program Olex2, version 1.2.<sup>37</sup> Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre, with numbers CCDC 1831809 (L1e), 1831810 (1a), 1831814 (1b), 1831811 (1c), 1831817 (1d) and 1831812 (1e). These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

#### 2.1.3 Alkane oxidation studies

A PerkinElmer Auto System gas chromatograph was utilised to analyse the products, which was equipped with a flame ionisation detector (FID) set at 260 °C. A Pona column (50 m x 0.20 mm x  $0.5\mu$ m) was employed for the separation of the products with the injector temperature set at 240 °C. All catalytic reactions were carried out in duplicate in 25 ml two-neck pear shaped flasks into which the reaction components were added and connected to a reflux condenser. Acetonitrile was employed as the solvent while cyclopentanone and *n*-octane was used as the internal standard and paraffin substrate respectively.

Two different types of oxidants were investigated i.e. *t*-butyl hydroperoxide (TBHP) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Furthermore, the total volume of the reaction mixture was kept constant at 5 ml. The catalyst was introduced in the form of a stock solution so that the number of moles of catalyst remained constant at  $9.56 \times 10^{-6}$  mol. A catalyst to substrate ratio of 1:100 was utilised whilst the substrate to oxidant ratio was varied in order to determine the optimum ratio. The optimum reaction times were different for the two oxidant systems. The reaction mixture was stirred in an oil bath maintained at 50 °C, after which an aliquot was removed, treated with an excess amount of PPh<sub>3</sub> and filtered through a silica plug prior to injecting 0.5 µl into the GC for analysis and quantification of the products.

The yield was calculated based on the total moles of product formed divided by the initial moles of substrate added into the reaction mixture and was expressed as a percentage, while the percentage selectivity was expressed as moles of each product divided by the total moles of all products.

#### 3. Results and discussion

#### 3.1 Synthesis and characterization of complexes

This study is based on five new complexes bearing neutral SNS ligands bound in tridentate pincer-type coordination modes to Cu(II) ions. A general synthetic route to the preparation of the ligands and complexes is presented in Scheme 1, of which ligands **L1a-c** and their Ni(II) complexes were recently reported<sup>32</sup>.



Scheme 1: General synthetic route for the preparation of the SNS ligands L1 and CuSNS complexes 1 where R = methyl (a), ethyl (b), butyl (c), cyclohexyl (d) and *t*-butyl (e).

Preparation of all the ligands (**L1a-e**) followed same procedure<sup>32</sup> and synthesis of the complexes involved addition of a solution of a ligand in methanol to a methanolic solution of CuCl<sub>2</sub>·2H<sub>2</sub>O. The observance of an instantaneous colour change served as the initial positive indicator of successful metal coordination. All the complexes were thus prepared, isolated, purified and fully characterised by IR, MS, elemental analysis, melting point determination and structural determination by single crystal X-ray diffraction (SCXRD). An examination of the IR results revealed some significant shifts in bands corresponding to the alkyl C–H stretch, bend and the C–N stretching frequencies (Table 1).<sup>38</sup> These shifts are indicative of successful coordination of the SNS ligands (**L1a-e**) to Cu(II) centres yielding corresponding complexes (**1a-e**). The most notable change in frequency is observed for the C–N stretch whereby shifts to lower wavenumbers were seen for the complexes in comparison to the unbound ligands. This result is a consequence of coordination of the ligand N-donor to the metal centre, which also correlates with the SCXRD for **L1e** and **1e** where a slightly longer C–N bond length was observed for the complex (**1.492** Å for **L1e** *vs* **1.496** Å for **1e**).

Compound	Frequency (cm <sup>-1</sup> )					
Compound	C-H stretch C-H bend		C-N stretch			
L1a	2843	1437	1110			
1a	2858	1441	1085			
L1b	2846	1453	1109			
1b	2866	1446	1087			

**Table 1:** Selected IR data for ligands L1a-e and the corresponding complexes 1a-e.

L1c 2872 1458	1116
<b>1c</b> 2861 1450	1088
L1d 2850 1447	1104
<b>1d</b> 2850 1447	1069
L1e 2862 1458	1105
<b>1e</b> 2862 1461	1071

ESI-MS analysis of the ligands and complexes gave results that are in line with calculated values. The ligand mass, together with a sodium adduct, is the most abundant ion, whereas for the complexes, the predominant species correspond to a mass of the ligand and copper only, with a loss of both chloride ligands, which dissociated during ionisation. Accurate combustion (CHN) analysis data in addition to sharp melting points confirmed isolation of all the complexes in high bulk purity. Due to the paramagnetic nature of complexes **1a-e**, no resolvable NMR data were possible, but detailed structural details were obtained from the SCXRD data presented below.

#### 3.2 Structural analysis by single crystal X-ray diffraction

It is interesting to note that all of the SNS ligands presented in this study exist as oils at room temperature, but an attempted complexation of ligand **L1e** to Ni(II) in EtOH via the commonly utilized nickel precursor Ni(PPh<sub>3</sub>)<sub>2</sub>Br<sub>2</sub> only yielded single crystals of a protonated bromide salt of **L1e**. The crystals were grown by layering a DCM solution of what was initially believed to be the SNS coordinated 'Ni complex' of **L1e** with Et<sub>2</sub>O. To our surprise, the crystal structure presented in Fig. 1 does not contain any coordinated metal. Instead, the N-donor atom of the SNS ligand was protonated via hydrogen transfer from the protic EtOH solvent used for the reaction, which was most likely catalysed by the metal precursor Ni(PPh<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>. The molecular structure of the salt (Fig. 1) shows that the ethylene linkers [C5, C6] and [C8, C9], and the central atoms defined by [C7, N1, H1 Br1] reside in two different planes that are nearly perpendicularly at an angle of 88.5°. The [C7, N1, H1, Br1] plane can also be considered as a C<sub>2</sub> rotation axis for the SNS skeletal backbone. Molecules of **L1e** exhibited non-classical hydrogen bonding (N–H…Br) separated by 2.191 Å, which is a relatively strong interaction in comparison to literature reports.<sup>39,40</sup> Hence, the crystal packing (II, Fig. 1), viewed along the *b*-axis, shows

intermolecular interactions in which two adjacent molecules are hydrogen bonded to two corresponding bromido ions (N–H…Br) in an almost perpendicular array.



**Figure 1:** Molecular structure (I) and crystal packing of the protonated salt of ligand **L1e** viewed along 010 (II) with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

For the metal complexes, single crystals of **1a** were grown from a MeOH solution, while concentrated solutions of **1b-1e** in MeOH or DCM layered with Et<sub>2</sub>O or heptane, yielded dark green crystals. The complexes crystallised with five coordinate ligand geometry around the Cu(II) centres. The compounds are in the monoclinic (**1a**, **1b** and **1e**), triclinic (**1c**) or orthorhombic (**L1e** and **1d**) crystal systems (Table 2) with packing diagrams for all complexes presented as supplementary materials (Fig S32 to S36).



**Figure 2:** Molecular structures of **1a** (I), **1c** (II) and **1e** (III) with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Table 2: Selected c	crystallographic and	structure refinement	data for	: L1e and com	plexes 1a-1e
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	L1e	1a	1b	1c	1d	1e
<b>F</b> · · · 1	C H D NG			C U CLC MG		
Empirical	$C_{13}H_{30}BrNS_2$	$C_7H_{17}CI_2CuNS_2$	$C_9H_{21}CI_2CUNS_2$	$C_{13}H_{29}Cl_2CuNS_2$	$C_{17}H_{33}Cl_2CuNS_2$	$C_{13}H_{29}Cl_2CuNS_2$
formula	244 41	212.00	241.05	207.06	450.04	207.06
Formula	344.41	313.80	341.85	397.96	450.04	397.96
weight	100(2)	100/2	172(0)	20((2))	100/2	20((2))
Temperature	100(2)	100(2)	1/3(2)	296(2)	100(2)	296(2)
(K)	0 4 1 1	N 11 1	1	m : 1: :		N 1'''
Crystal	Orthorhombic	Monoclinic	Monoclinic	Iriclinic	Orthorhombic	Monoclinic
system	<b>DO 0 0</b>			<b>N</b> -	D.	
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2	$P2_1/n$	$P2_1/n$	$P_{\overline{1}}$	Pbca	$P2_1/c$
a (A)	10.1665(15)	7.7103(4)	12.8374(4)	8.58240(1)	12.1895(6)	15.0660(3)
b (A)	27.674(4)	12.1139(7)	14.2641(5)	14.5582(2)	21.8132(10)	9.7401(2)
c (A)	6.3937(9)	13.6506(8)	16.1896(3)	15.4678(2)	31.6331(14)	13.5252(2)
α (°)	90	90	90	105.5750(1)	90	90
β (°)	90	101.201(2)	91.293(2)	98.6340(1)	90	110.5780(1)
γ (°)	90	90	90	96.7680(1)	90	90
Volume (Å <sup>3</sup> )	1798.9(4)	1250.70(12)	2963.79(15)	1814.99(4)	8411.0(7)	1858.11(6)
Z	4	4	4	4	16	4
$\rho_{calc}$ (g/cm <sup>3</sup> )	1.272	1.6664	1.532	1.4563	1.4215	1.4225
μ (mm <sup>-1</sup> )	2.502	2.466	2.088	1.716	1.491	1.676
F(000)	728	647.6	1416.0	839.7	3806.8	839.6
Crystal size	0.290  imes 0.180  imes	0.641  imes 0.34  imes	0.210  imes 0.140  imes	0.45  imes 0.25  imes	0.844  imes 0.656  imes	0.246  imes 0.092  imes
(mm <sup>3</sup> )	0.140	0.269	0.090	0.25	0.42	0.078
20 range for	4.268 to 56.578	4.54 to 56.8	7.616 to 55.758	4.6 to 57.22	2.58 to 50.74	5.08 to 56.76
data						
collection (°)						
Index ranges	$-11 \le h \le 13$ ,	$-10 \le h \le 10$ ,	-16≤ h ≤16,	$-11 \le h \le 11$ ,	$-14 \le h \le 14$ ,	$-20 \le h \le 19$ ,
-	$-18 \le k \le 36$ ,	$-16 \le k \le 15$ ,	$-18 \le k \le 18$ ,	$-19 \le k \le 19$ ,	$-26 \le k \le 26$ ,	$-12 \le k \le 13$ ,
	$-8 \le l \le 5$	-17≤1≤18	-21≤1≤21	$-20 \le l \le 20$	$-37 \le 1 \le 38$	$-17 \le l \le 17$
Reflections	8366	28014	164198	34856	170453	29195
collected						
Independent	3932 [R(int) =	3113 [R(int) =	7054 [R(int) =	9196 [R(int) =	7720 [R(int) =	4604 [R(int) =
reflections	0.0240]	0.0237]	0.0604]	0.0181]	0.08081	0.0271]
Data / restraints	3932 / 0 / 155	3113/0/121	7054 / 0 / 277	9199 / 0 / 369	7720 / 0 / 429	4604 / 0 / 189

parameters	1.040	1.016	1 109	1 055	1 070	1 051
$\frac{-2}{2}$	1.049	1.010	1.108	1.055	1.070	1.031
fit on F						
Final R	R1 = 0.0273,	R1 = 0.0180,	R1 = 0.0289,	R1 = 0.0267,	R1 = 0.0415,	R1 = 0.0242,
indices [I	wR2 = 0.0532	wR2 = 0.0493	wR2 = 0.0575	wR2 = 0.0684	wR2 = 0.0879	wR2 = 0.0573
>=2σ (I)]						
Final R	R1 = 0.0317,	R1 = 0.0184,	R1 = 0.0450,	R1 = 0.0296,	R1 = 0.0648,	R1 = 0.0285,
indices (all	wR2 = 0.0549	wR2 = 0.0495	wR2 = 0.0638	wR2 = 0.0711	wR2 = 0.1014	wR2 = 0.0592
data)						7
Largest diff.	0.43 and -0.69	0.37 and -0.61	0.54 and -0.38	1.96 and -1.07	0.82 and -0.62	0.61 and -0.28
peak and hole						
$(e.Å^{-3})$						

Table 3: Selected bond lengths (Å) and bond angles (°) for 1a, 1c and 1e.

Bond lengths (Å)	1a	1c	1e
N1-Cu1	2.0741(12)	2.0808(16)	2.0781(15)
S1-Cu1	2.5632(4)	2.5552(5)	2.5178(5)
S2-Cu1	2.3495(4)	2.3474(5)	2.4027(5)
Cl1–Cu1	2.2623(4)	2.2637(5)	2.2736(5)
Cl2–Cu1	2.2968(4)	2.2981(5)	2.2964(5)
Bond angles (°)			
S1-Cu1-S2	109.594(14)	112.938(17)	123.036(17)
N1-Cu1-S1	83.99(3)	86.31(4)	85.33(4)
N1-Cu1-S2	86.40(4)	83.31(5)	83.73(4)
N1-Cu1-Cl1	172.19(4)	170.61(5)	170.77(4)
N1-Cu1-Cl2	93.52(3)	92.41(5)	92.54(4)

ORTEP diagrams showing the molecular structures of complexes **1a**, **1c** and **1e**, presented in Fig. 2, show the SNS ligands coordinated in the expected tridentate fashion around each Cu(II) centre. Previous results on a NiSNS complex based on ligand **L1c** we reported showed that the complex displayed six coordinate, distorted octahedral geometry around the Ni(II) centre.<sup>32</sup> Furthermore, analogous CuSNS complexes reported by Blomenkemper *et al.* and Hajifatheali *et al.*.<sup>24,25</sup> showed five-coordinate distorted square pyramidal geometry of ligands. Hence, we determined the tau parameter for complexes **1a**, **1c** and **1e** to determine the actual geometry of each Cu(II) coordination centre. It was found as  $\tau = 1.04$ , 0.96 and 0.80 for **1a**, **1c** and **1e** respectively, indicative of distorted trigonal bipyramidal arrangement of ligands. In all three complexes, the arrangements involve axially coordinated (N-donor and Cl1) and equatorially

coordinated Cl2 and two S-donors. For ease of comparison, structurally important bond lengths and angles for **1a**, **1c** and **1e** are presented in Table 3. The 'bite angle', defined by S1–Cu1–S2, is acute for **1a** (109.594(14)°), but much more open for **1c** (112.938(17)°) and **1e** (123.036(17)°) implying a more accessible metal centre in the latter. This trend establishes a direct correlation between steric size of the S-donor substituents and the bite angle, which may be related to the ability of the central metal to coordinate and accommodate substrates during catalytic transformations.<sup>19,24,41</sup> The bond lengths corresponding to N1–Cu1, S1–Cu1 and S2–Cu1 are comparable for **1a** and **1c**, however, for complex **1e** the S1–Cu1 bond is slightly shorter at 2.5178(5) Å, whilst a longer S2–Cu1 bond is noted at 2.4027(5) Å. Overall, the S1–Cu1 bond for all three complexes is significantly longer than reported literature values for related CuSNS complexes, which are in the range of 2.3168-2.3625 Å.<sup>24</sup>

Selected bond lengths and angles for **1b** and **1d** are shown in Table 4. Complex **1b** crystallises with two independent molecules in its asymmetric unit cell, identified as fragments A and B (Fig. 3). Although both fragments showed similar bond parameters, a slightly wider bite angle of  $110.54(2)^{\circ}$  was observed for fragment A in comparison to fragment B, with a S1–Cu1–S2 angle of  $107.66(2)^{\circ}$ . The coordination geometry in complex **1b** is similar to those of aforementioned complexes, with trigonal bipyramidal configuration for both fragments ( $\tau = 1.02$  and 1.09 for A and B respectively). Furthermore, the axial (N1, Cu1, Cl1) and the equatorial (S1, Cu1, S2, Cl2) planes intersect at an average angle of  $85.05^{\circ}$  for the two fragments, which contributed to the distorted geometries observed around the metal centres.

 Table 4: Selected bond lengths (Å) and bond angles (°) for fragments A and B of complexes 1b and 1d.

Bond lengths (Å)	1b		1d	
	Α	В	Α	В
N1-Cu1	2.0604(15)	2.0830(16)	2.076(3)	2.084(3)
S1–Cu1	2.6525(6)	2.6020(6)	2.3688(10)	2.5432(11)
S2-Cu1	2.3620(5)	2.3529(6)	2.3733(10)	2.3852(11)
Cl1–Cu1	2.2988(5)	2.2868(5)	2.4699(10)	2.2798(10)
Cl2-Cu1	2.2531(6)	2.2676(6)	2.2493(10)	2.2928(10)
Bond angles (°)				

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S1-Cu1-S2	110.542(19	107.656(19)	161.36(4)	118.37(4)
N1-Cu1-S1	82.44(4)	85.94(5)	85.00(9)	83.66(10)
N1-Cu1-S2	86.41(5)	82.76(5)	84.47(9)	84.27(9)
N1-Cu1-Cl1	171.89(5)	172.77(5)	94.27(9)	171.02(9)
N1-Cu1-Cl2	93.36(5)	93.98(5)	152.38(9)	92.59(9)



**Figure 3:** Molecular structure of **1b** showing two independent molecules (A and B) in the asymmetric unit cell with hydrogen atoms omitted and molecule B reoriented for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Complex **1d** (Fig. 4) also crystallised with two crystallographically independent molecules (A and B) in the asymmetric unit cell, but each fragment has a few unique features. For instance, the geometry around the metal centre in fragment A is a distorted square pyramid ( $\tau = 0.15$ ), in which the basal plane is occupied by N1A, S1A, S2A and Cl2A, whilst Cl1A occupied the apical position. This is comparable in conformation to a similar CuSNS complex reported with bulkier bromide ligands and a secondary amine backbone, as a consequence of which the reported bite angle was more obtuse at 170.58(2)° vs 161.36(4)° for fragment A.<sup>42</sup> In fragment B, a distorted trigonal bipyramidal geometry was displayed ( $\tau = 0.88$ ), where N1B and Cl1B occupy the axial positions forming an angle of 171.02(9)°, whilst S1B, S2B and Cl2B reside in the equatorial plane. In comparison to **1a**, **1b** and **1c**, a notably wider bite angle was observed for **1d** and this may be attributed to the bulkier cyclohexyl substituents in the chair conformation.



**Figure 4:** Molecular structure of **1d** showing the two independent molecules (A and B) in the asymmetric unit cell, with one conformation of the disordered cyclohexyl group displayed, hydrogen atoms omitted and molecule B reoriented for clarity. Thermal ellipsoids are drawn at the 50% probability level.

#### 3.3 Oxidation of *n*-octane

All the prepared complexes were applied as catalysts in the oxidation of *n*-octane using either TBHP or  $H_2O_2$  as oxidant. All reactions were conducted in air under atmospheric pressure and a reaction temperature of 50 °C. Various octane to oxidant ratios were tested in order to optimise the quantity of oxidant required. Ratios of 1:12 and 1:9 for octane:TBHP and octane: $H_2O_2$  respectively, were determined as optimum for the best balance between product yield and selectivity. Blank reactions in the absence of a catalyst produced yields of ca. 1% in 24 h for the system with TBHP as the oxidant, whilst no conversion was observed in the absence of a catalyst at the optimum reaction time for the  $H_2O_2$  system (1 h). Conversions and product distribution of the catalytic systems were benchmarked against a simple CuCl<sub>2</sub> salt in order to determine the influence of the SNS ligand system on Cu catalysed oxidation of *n*-octane.

For the **1**/TBHP systems, both the conversion and product distribution were comparable to that of the CuCl<sub>2</sub> precursor (see Fig. S37 and S38). The results imply that in all cases, the addition of TBHP led to ligand dissociation. Despite the absence of any ligand effect with TBHP as the source of oxidant, a reasonable total yield of ~15% was recorded, which is higher than some of our earlier results reported in the literature.<sup>43-45</sup> A closer analysis of the distribution of products indicates that the ketones represent the major products. Furthermore, it was found that the reaction does not proceed in the presence of TEMPO, a common radical inhibitor, thus suggesting a radical initiated pathway as the most plausible mode of action.

		Selectivity (%)			
Catalyst	Yield to C-8 oxygenates (%)	-ol <sup>b</sup>	-one <sup>c</sup>	<b>C</b> (1) <sup>d</sup>	
1a	27	76	6	18	
1b	34	74	6	20	
1c	23	77	5	18	
1d	36	78	5	18	
1e	26	76	7	18	
CuCl <sub>2</sub>	34	75	7	19	

Table 5: Catalytic oxidation of *n*-octane at 50 °C with H<sub>2</sub>O<sub>2</sub> as oxidant.<sup>a</sup>

<sup>a</sup> All reactions were conducted for a time period of 1 h. Catalyst:octane: $H_2O_2 = 1:100:900$ .

<sup>b</sup> 2-, 3- and 4-octanol. <sup>c</sup> 2-, 3- and 4-octanone. <sup>d</sup> 1-octanol and octanoic acid

The result obtained for the 1/H<sub>2</sub>O<sub>2</sub> systems (Table 5) is much different to the reactions with TBHP. An optimum octane to TBHP ratio of 1:9 was established with the highest yield to C-8 oxygenates obtained at 1 h reaction time. From the results, it is apparent that the complexes gave relatively high combined yields (23-36%) of C-8 oxygenate products. The copper salt was also quite active with a calculated yield of 34% to C-8 oxygenates. It is possible that a lag phase initially occurs, where the rate of ligand dissociation varies for each of the catalysts, hence the disparity in the yields obtained.

Analysis of product distribution profiles revealed that alcohol products predominate with the  $1/H_2O_2$  catalytic systems as opposed to the results of the 1/TBHP systems where ketones were more abundant. This can be attributed to the much shorter reaction time of 1 h for the  $H_2O_2$ 

reactions compared to the 24 h for TBHP whence the over oxidation of alcohols to ketones is more likely. Furthermore, no distinction in the product selectivity was observed amongst the catalysts in comparison to the uncomplexed CuCl<sub>2</sub> salt. This suggests that the ligands have no influence on the activity and selectivity of the catalysts, possibly due to their instability under the oxidizing conditions. The X-ray crystal structural data of complex series **1** showed some degree of asymmetry and/or disorder, brought about by the flexible backbone, which may be significant contributing factors to the instability of the complexes in oxidizing environments.

In spite of the apparent lack of direct ligand based catalyst control, the significance of these results is best appreciated when it is benchmarked against previous studies based on cobalt and nickel complexes containing related SNS ligands.<sup>12,32</sup> Yields of up to 10% and 23% were obtained with the NiSNS and CoSNS catalysts respectively at 24 h using TBHP as the oxidant. It is noteworthy that the copper system reported herein employ a much greener oxidant ( $H_2O_2$ ) working at a considerably reduced reaction time (1 h) and yielding much higher conversions of *n*-octane (up to 36% yield to C-8 products). This clearly demonstrates that copper is a much better choice of metal over either cobalt or nickel for the oxy-functionalisation of *n*-octane. Moreover, the prevalent product group is the alcohols as opposed to the over oxidised ketones observed with the TBHP (Ni or Co) systems.

From this study it is evident that the architecture of the ligand backbone, as well as the choice of the metal that make up the catalyst, need to be carefully considered. Although the ligands were flexible, they were rendered unstable under the conditions employed for the catalysis, yet copper has shown significant enhancements over previously studied metals. Therefore, further investigation is required for designing a flexible but stable ligand backbone that could potentially improve the catalytic activity of the Cu(II) systems even further.

# 4. Conclusion

In this work, pincer-type SNS ligands and their respective new copper complexes were successfully synthesized using simple procedures. Characterisation by various techniques confirmed the structural composition and bulk purity of all the prepared complexes. All the complexes existed as mononuclear species characterised by five coordinate ligand geometry

around each Cu(II) centre. All the complexes were applied as catalysts for the oxidation of *n*-octane using TBHP and H<sub>2</sub>O<sub>2</sub> as oxidants. The Cu(II)/H<sub>2</sub>O<sub>2</sub> catalyst systems produced yields of 23-36% with predominant C-8 alcohol selectivity. Hence, this study serves to extend our understanding on the role of the SNS backbone on catalytic activity in *n*-octane oxidation. Lack of steric rigidity of the methyl N-substituent rendered the resulting complexes unhindered, flexible and unstable under the harsh oxidising environment of the catalytic process. Hence, further exploration is still needed to achieve a balanced structure/activity relationship for complexes bearing the modular SNS ligand backbone.

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#### Highlights

A series of flexible SNS pincer ligands with a methyl functionality on the nitrogen backbone and a variation of substituents on the S-donor atoms were prepared.

Coordination of the ligands to copper, using CuCl<sub>2</sub>·2H<sub>2</sub>O as the metal precursor, yielded fivecoordinate complexes, which were fully characterised.

All the complexes were found to be catalytically active in the oxidation of *n*-octane using  $H_2O_2$  as the oxidant.

Relatively high yields to C-8 oxygenates were obtained at one hour with high selectivity to the alcohol products.