Synthesis of Fe and Cu metal complexes derived from ‘SNS’ Pincer type ligands and their efficient catalyst precursors for the chemical fixation of CO₂

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Abstract. Two novel tridentate SNS pincer type ligands, 2,6-bis[(2'-methoxyphenyl)thio]methylpyridine (**L1**) and 2,6-bis[(2'-chlorophenyl)thio]methylpyridine (**L2**), each possessing two sulfur and one nitrogen donor functionalities (SNS), based on 2,6-bis(thioether)pyridine ligands were prepared and metallised with CuCl₂ · 2H₂O and FeCl₂ · 4H₂O metal salts. Two new unanticipated complexes were obtained from the **L2** ligand, the dimeric bidentate Cu(I) complex [Cu₂(κ²-**L2**)₂Cl₂] and tridentate Fe(II) complex [Fe(κ³-**L2**)Cl₂] while two new tridentate pincer-type complexes M(κ³-**L1**)Cl₂] (M = Cu, Fe) were formed from the **L1** ligand. It was observed that the structure of this Cu(I) complex has a tetrahedral geometry using single crystal X-ray diffraction analysis. In addition, catalytic properties of metal complexes towards the formation of cyclic carbonates from CO₂ and epoxides were investigated. The less sterically hindered Fe(II) complex with the **L1** ligand [Fe(κ³-**L1**)Cl₂] (**2**) showed the best catalytic activity. Several parameters including temperature, time, epoxide identity and CO₂ pressure were investigated to find the optimum catalytic reaction conditions. Moreover, DFT studies of these compounds are presented in the study.

Keywords. SNS pincer complexes; CO₂; catalysts; single crystal X-ray diffraction; density Functional Theory.

1. Introduction

Pincer-type complexes from bis(thioether) ligands surrounding a central pyridine group have attracted much interest because of their beneficial activities in a wide range of catalytic processes such as olefin hydroamination, alkene hydrogenations, Heck and Suzuki couplings, etc.^{1,2} Cu(II) and Fe(II) metal complexes with such ligands are being extensively used as catalysts for many important processes.³ Fundamental studies on the

nature of the pincer ligands and the electronic properties of their complexes on catalytic activities are therefore of interest.

The general aim for the recent upswing in studies of the catalytic properties of these pincer compounds is to obtain efficient catalysts for different applications. A good catalyst should be (i) easily synthesized, (ii) the catalyst-forming ligand must be stable, flexible, usable and easily adjustable, and (iii) inexpensive. For broader use, the cost issue can become even more

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Scheme 1. Synthesis of cyclic organic carbonates.

important. Due to their ideal disposition of electron donor atoms, pincer ligands can form complexes with various transition metals. Both pincer compounds and the resulting metal complexes have a range of interesting properties including catalytic potential,⁴ electrochemical features,^{5–8} biochemical applications,^{9–13} interaction between organic molecules and metal surfaces^{14–16} and polymerization¹ that all have been investigated previously.

The largest contributor to anthropogenic greenhouse gas emission is attributable to carbon dioxide (CO₂) and this is closely connected to global climate change.¹⁷ Conversely, carbon dioxide is a renewable carbon source because it is both cheap, abundant and non-toxic.^{18,19} Chemical production using carbon dioxide as raw material seems to be quite attractive in terms of value-added products. Some pathways of CO₂ conversion include CO₂ coupling with alkenes, epoxides or alkynes, to produce functionalized products.²⁰ However, among the most efficient of carbon dioxide conversions, cyclic carbonate synthesis can be demonstrated by the incorporation of carbon dioxide and epoxides (Scheme 1).^{21,22} Hence, the utilization of CO₂ as a C1-building block in organic synthesis and industrial processes has recently received great interest and is being studied widely.^{23,24}

In particular, it has a wide range of industrial use, including five-membered cyclic carbonates, electrolytes in lithium-ion batteries, aprotic polar solvents, biomedical applications, organic synthetic intermediates, plastics and monomer units, raw materials for polycarbonates.^{21,25,26} Many different catalysts have been improved for the synthesis of cyclic organic carbonates from CO₂ and epoxides. Among these are several heterogenized and homogeneous salen complexes,²⁷ metal complexes,²⁸ organic bases,²⁹ alkali metal halides,³⁰ zeolites,³¹ metal oxides,³² and ionic liquids.³³

In this study, two ligands (**L1** and **L2**) and their Fe^{II}, Cu^{II} and Cu^I metal complexes were synthesized and characterized *via* elemental analysis, mass spectrometry, spectroscopy (e.g., NMR, UV-Vis and

FT-IR spectroscopy) and, in the case of **L1** and the Cu complex of **L2**, by single crystal X-ray diffraction analysis. The four reported metal complexes are [M(κ^3 -**L1**)Cl₂] (M = Cu, **1**; Fe, **2**), [Cu₂(κ^2 -**L2**)₂Cl₂] (**3**), [Fe(κ^3 -**L2**)Cl₂] (**4**) and they were employed as catalysts for the production of cyclic carbonates from epoxides and CO₂. The most active catalyst (**2**) was used and optimization studies were then performed by investigating changes to different reaction parameters including epoxide variation, reaction time, temperature and pressure. DFT studies of these compounds compliment these efforts.

2. Experimental

2.1 Materials and methods

All reactions involving 2,6-bis[(2'-methoxyphenyl)thio]methylpyridine (**L1**) and 2,6-bis[(2'-chlorophenyl)thio]methylpyridine (**L2**) ligands were carried out under a nitrogenous atmosphere. All chemicals and solvents used in the experiments were assured from Turkey's representative of Sigma Aldrich (St. Louis, MO) and Fluka (Buchs, Switzerland), which were used without any further purification. Ultraviolet-visible (UV-Vis) spectrums of compounds in DMF were recorded by a PG Instruments (UK) T80+UV-visible spectrophotometer. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra of compounds were measured in DMSO-d₆ by using a Bruker High-Performance Digital FT-NMR (400 MHz) spectrometer. Tetramethylsilane (TMS) was used as an internal reference. FT-IR spectra of compounds were measured in the range of 4000–400 cm⁻¹ by using a Perkin Elmer Spectrum 100 FT-IR Spectrometer (universal ATR sampling accessory). The elemental analysis for C, H, N and S were performed on a Thermo Scientific Flash EA 2000 CHNS analyzer. Also, the mass spectra were recorded using an ABSciex (Framingham, MA) 3200 QTrap system liquid chromatography with tandem mass spectroscopy (LC/MS/MS) in the electrospray mode. The yields of cyclic carbonates were determined by gas chromatography (GC) using an Agilent 7820A Gas Chromatograph, equipped with a 30 m HP-5 column. The GC conditions for the product analysis were: Injector Port Temperature: 250 °C;

Column Temperature: Initial temperature: 60 °C; Gradient Rate: 18 °C/min (3 min); Final Temperature: 220 °C (10 min.); FID: 300 °C; Flow Rate: 25 mL/min (N₂); Split Ratio: 1/30.

2.2 Crystallographic analysis

2.2a Crystal structure determination: The single crystal X-ray data for 2,6-bis[(2'-methoxyphenyl)thio]methylpyridine (**L1**) (C₂₁H₂₁NO₂S₂) and copper complex [Cu(κ^2 -2,6-bis[(2'-chlorophenyl)thio]methylpyridine)Cl] [Cu₂(κ^2 -**L2**)₂Cl₂] (**3**)(C₁₉H₁₅Cl₃CuNS₂) were collected by an Agilent Diffraction Xcalibur, EOS diffractometer.³⁴ Data collection was carried out at 293(2) K.³⁵ The structure was solved via Olex2 with the ShelXT structure solution program³⁶ by using Direct Methods and refined with the ShelXL refinement package³⁶ via Least Squares minimization. Details can be found in Table S1, Supplementary Information.

2.3 Molecular calculation

The geometry optimization, molecular energy, vibrational spectra, Mulliken charges and Molecular Electrostatic Potential calculations of the ligands and their complexes performed with Gaussian 09W software implemented Becke's hybrid functional B3LYP/6-31g(d) in the gas phase.^{37–39} The structure and vibrational band assignments were visualized by using the Gauss-View 5 program.⁴⁰

2.4 Synthesis of the ligands

2.4a Synthesis of 2,6-Bis[(2'-methoxyphenyl)thio]methylpyridine (L1**):** In the presence of potassium iodide (0.166 g, 1 mmol) and potassium carbonate (0.542 g, 4 mmol), 2-methoxybenzenethiol (0.280 g, 2 mmol) was added to solution of 2,6-bis(chloromethyl)pyridine (0.176 g, 1 mmol) in 30 mL DMF. The reaction mixture was stirred at 80 °C over 48 h. Then, the reaction mixture was poured into iced water and extracted three times with chloroform. The organic phase was completely evaporated to dryness. The compound was purified by crystallization using slow vapor diffusion of Et₂O into a THF solution of compound **L1**. This ligand was obtained as a yellow crystalline solid compound (90%). M.p. 73–74 °C. IR, (ATR) cm⁻¹: 3062 (C-H)_{aromatic}, 2988, 2955, 2938 (C-H)_{aliphatic}, 1571 (C=N)_{pyridine}, 748 (C-S-C); ¹H-NMR DMSO-d₆, 400 MHz): δ 7.63 (t, 1H, *J* = 8 Hz, H-4), 7.31 (d, 2H, *J* = 8 Hz, H-11), 7.27 (d, 2H, *J* = 8 Hz, H-3), 7.15 (t, 2H, *J* = 8 Hz, H-9), 6.96 (d, 2H, *J* = 8 Hz, H-8), 6.86 (t, 2H, *J* = 8 Hz, H-10), 4.23 (s, 4H, H-5), 3.80 (s, 6H, H-12). ¹³C-NMR (DMSO-d₆, 400 MHz): δ 157.70 (C-2), 156.54 (C-7), 137.79 (C-4), 128.26 (C-6), 127.02 (C-8), 124.85 (C-11), 122.75 (C-10), 121.50 (C-9), 111.05 (C-3), 37.35 (C-5), 56.11 (C-12); UV-Vis (DMF) $\lambda_{\max}$ (Abs): 285 (1.039), 275 (0.929), 269 (0.898) nm. ESI-MS, *m/z*: 384.7 [(**L1**) + H]⁺. Anal. Calc. For C₂₁H₂₁NO₂S₂ (383.53): C, 65.76; H, 5.52;

N, 3.65; S, 16.72%. Found: C, 65.55; H, 5.47; N, 3.66; S, 16.87%.

2.4b Synthesis of the 2,6-Bis[(2'-chlorophenyl)thio]methylpyridine (L2**):** In the presence of potassium iodide (0.166 g, 1 mmol) and potassium carbonate (0.542 g, 4 mmol), 2-chlorothiophenol (0.289 g, 2 mmol) was added to solution of 2,6-bis(chloromethyl)pyridine (0.176 g, 1 mmol) in 30 mL DMF. The reaction mixture was stirred at 80 °C over 48 h. The compound was purified using slow vapor diffusion of Et₂O into a THF solution of compound **L2**. This ligand was obtained as a yellow color viscous oil compound (71%). IR, (ATR) cm⁻¹: 3058 (C-H)_{aromatic}, 2961, 2925 (C-H)_{aliphatic}, 1572 (C=N)_{pyridine}, 740 (C-S-C); ¹H-NMR DMSO-d₆, 400 MHz): δ 7.72 (t, 1H, *J* = 8 Hz, H-4), 7.53 (d, 2H, *J* = 10.4 Hz, H-8), 7.43 (d, 2H, *J* = 10.4 Hz, H-11), 7.38 (d, 2H, *J* = 10.4 Hz, H-3), 7.25 (t, 2H, *J* = 10.4 Hz, H-10), 7.16 (t, 2H, *J* = 10.4 Hz, H-9), 4.38 (s, 4H, H-5). ¹³C-NMR (DMSO-d₆, 400 MHz): δ 156.59 (C-2), 138.33 (C-7), 136.14 (C-4), 131.16 (C-6), 129.61 (C-8), 128.07 (C-11), 126.99 (C-10), 122.20 (C-3), 37.52 (C-5); UV-Vis (DMF) $\lambda_{\max}$ (Abs): 360 (0.030), 290 (0.362), 275 (0.857), 270 (1.093) nm. ESI-MS, *m/z*: 393.8 [(**L2**) + H]⁺. Anal. Calc. For C₁₉H₁₅Cl₂NS₂ (392.37): C, 58.16; H, 3.85; N, 3.57; S, 16.34%. Found: C, 58.09; H, 4.12; N, 3.60; S, 15.93%.

2.4c Synthesis of [Cu(κ^3 -L1**)Cl₂] · 2H₂O (**1**):** In a 100 mL round-bottomed flask 2,6-bis[(2'-methoxyphenyl)thio]methylpyridine (**L1**) (0.379 g, 0.99 mmol) was added in 25 mL of THF to give a yellow solution. The reaction mixture was heated to 70 °C with stirring activated. CuCl₂ · 2H₂O (0.168 g, 0.99 mmol) in 10 mL MeOH was added. The reaction mixture was held 70 °C with stirring activated for 30 min. The product was filtered off, washed with Et₂O and cold methanol, and dried in vacuum to obtain as a dark brown solid compound. The compound was purified by crystallization from a mixture of THF/MeOH. Yield: 0.334 g (61%). M.p. 146–147 °C. IR, (ATR) *v*, cm⁻¹: 3406 (O-H), 3062 (C-H)_{aromatic}, 3010, 2973, 2938 (C-H)_{aliphatic}, 1571 (C=N)_{pyridine}, 745 (C-S-C), 573 (M-N); UV-Vis (DMF) $\lambda_{\max}$ (Abs): 360 (0.038), 285 (1.052), 275 (1.008) nm; ESI-MS, *m/z*: 554.2 [Cu(**L1**) + 2Cl + 2H₂O + 2H]⁺, 522.5 [Cu(**L1**) + 2Cl]⁺. Anal. Calc. For C₂₁H₂₅Cl₂CuNO₄S₂ (554.01): C, 45.53; H, 4.55; N, 2.53; S, 11.58. Found: C, 45.95; H, 4.47; N, 3.02; S, 11.12%.

2.4d Synthesis of [Fe(κ^3 -L1**)Cl₂] · C₄H₈O (**2**):** In a 100 mL round-bottomed flask 2,6-bis[(2'-methoxyphenyl)thio]methylpyridine (**L1**) (0.384 g, 1 mmol) was added in 25 mL of THF to give a yellow solution. The reaction mixture was heated to 70 °C with stirring activated. FeCl₂ · 4H₂O (0.198 g, 1 mmol) in 10 mL MeOH was added. The reaction mixture was held 70 °C with stirring activated for 30 min. The product was filtered off, washed with Et₂O and cold methanol, and dried in vacuum to obtain a dark brown viscous oil. The complex was purified using slow vapor diffusion of Et₂O into a THF solution of complex **2**. Yield: 0.436 g

(75%). IR, (ATR) ν , cm^{-1} : 3064 (C-H)_{aromatic}, 2938, 2883, 2837 (C-H)_{aliphatic}, 1579 (C=N)_{pyridine}, 747 (C-S-C), 573 (M-N); UV-Vis (DMF) λ_{max} (Abs): 481 (0.036), 360 (0.133), 311 (0.344), 285 (0.953), 275 (0.873), 270 (0.813) nm; ESI-MS, m/z : 582.2 $[\text{Fe}(\text{L1}) + 2\text{Cl} + \text{C}_4\text{H}_8\text{O}]^+$. Anal. Calcd. $\text{C}_{25}\text{H}_{29}\text{Cl}_2\text{FeNO}_3\text{S}_2$ (582.38); C, 51.56; H, 5.02; N, 2.40; S, 11.01. Found: C, 51.39; H, 4.96; N, 2.14; S, 10.72%.

2.4e Synthesis of $[\text{Cu}_2(\kappa^2 - \text{L2})_2\text{Cl}_2]$ (3**):** In a 100 mL round-bottomed flask (2,6-bis{[(2'-chlorophenyl)thio]methyl}pyridine) (**L2**) (0.280 g, 0.714 mmol) was added in 25 mL of THF to give a yellow solution. The reaction mixture was heated to 70 °C with stirring on. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.121 g, 0.714 mmol) in 10 mL MeOH was added. The reaction mixture was held at 70 °C with stirring activated for 30 min. The solid product was removed by filtration, washed with cold methanol and Et_2O , was recrystallized in THF-methanol (4:1) and dried in vacuum to obtain a dark yellow crystalline solid. Yield: 0.150 g (43%). M.p. 152–153 °C. IR, (ATR) ν , cm^{-1} : 3059 (C-H)_{aromatic}, 2973, 2878 (C-H)_{aliphatic}, 1563 (C=N)_{pyridine}, 747 (C-S-C), 573 (M-N); UV-Vis (DMF) λ_{max} (Abs): 360 (0.019), 275 (0.706), 270 (0.895) nm; ESI-MS, m/z : 490.94 $[\text{Cu}(\text{L2}) + \text{Cl}]^+$. Anal. Calcd. $\text{C}_{38}\text{H}_{30}\text{Cl}_6\text{Cu}_2\text{N}_2\text{S}_4$ (982.66); C, 46.44; H, 3.08; N, 2.85; S, 13.05. Found: C, 46.59; H, 2.93; N, 2.99; S, 13.08%.

2.4f Synthesis of $[\text{Fe}(\kappa^3 - \text{L2})\text{Cl}_2] \cdot \text{C}_4\text{H}_8\text{O}$ (4**):** In a 100 mL round-bottomed flask (2,6-bis{[(2'-chlorophenyl)thio]methyl}pyridine) (**L2**) (0.370 g, 0.943 mmol) was added in 25 mL of THF to give a yellow solution. The reaction mixture was heated to 70 °C with stirring activated. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.187 g, 0.943 mmol) in 10 mL of MeOH was added. The reaction mixture was held at 70 °C with stirring activated for 30 min. The compound was purified using vapor diffusion of Et_2O into a THF solution of complex **4**. Complex **4** was obtained as reddish-brown viscous oil. Yield: 0.418 g (75%). IR, (ATR) ν , cm^{-1} : 3059 (C-H)_{aromatic}, 2928, 2875 (C-H)_{aliphatic}, 1572 (C=N)_{pyridine}, 742 (C-S-C), 570 (M-N); UV-Vis (DMF) λ_{max} (Abs): 491 (0.065), 359 (0.112), 310 (0.242), 275 (1.089), 270 (1.297) nm; ESI-MS, m/z : 591.1 $[\text{Fe}(\text{L2}) + 2\text{Cl} + 2\text{C}_4\text{H}_8\text{O}]^+$. Anal. Calcd. $\text{C}_{23}\text{H}_{23}\text{Cl}_4\text{FeNOS}_2$ (591.22); C, 46.72; H, 3.92; N, 2.37; S, 10.85. Found: C, 46.70; H, 3.22; N, 2.97; S, 11.91%.

2.5 General procedure for the cycloaddition of epoxides to CO_2

A 25 mL stainless pressure reactor was charged with metal complex (4.5×10^{-5} mol), epoxide (4.5×10^{-2} mol), and DMAP (9×10^{-5} mol). The reaction vessel was placed under constant pressure of CO_2 for 2 min to allow the system to equilibrate and then the autoclave was charged with CO_2 to the desired pressure. The reaction mixture was then heated to the desired temperature. The pressure was kept constant during the reaction. After the desired reaction time the vessel was cooled to 5–10 °C in an ice bath. The pressure was released

by venting the excess gases. The yields of the corresponding cyclic carbonates were determined by using an Agilent 7820A Gas Chromatograph.

3. Results and Discussion

3.1 Synthesis and characterization of ligands

The reaction of either 2-methoxybenzenethiol or 2-chlorothiophenol with 2,6-bis(chloromethyl)pyridine in DMF led to the isolation of two new bis(arylthioether) SNS pincer type ligands, 2,6-{[bis(2-methoxyphenyl)sulfanyl]methyl}pyridine (**L1**) or 2,6-{[bis(2-chlorophenyl)sulfanyl]methyl}pyridine (**L2**), respectively (Scheme 2). These potentially tridentate species are soluble in common organic solvents such as ethanol, methanol, DMF, THF and chloroform. The compounds were characterized using FT-IR, UV-Vis, mass spectrometry and NMR spectroscopic techniques and elemental analysis. While **L1** was isolated as a crystalline solid, **L2** was obtained as a viscous liquid at room temperature. In addition, **L1** was subjected to single crystal X-ray analysis.

^1H -NMR and ^{13}C -NMR spectra of ligands were recorded in DMSO-d_6 . In the spectra of these compounds, the aromatic protons were observed as multiplets between δ 7.63–6.86 ppm (11H) for **L1** and 7.72–7.16 ppm (11H) for **L2**. Signals for the methylene– CH_2 –S– groups were observed as singlets at δ 4.23 ppm (4H) (**L1**) and δ 4.38 ppm (4H) (**L2**). Finally, the methoxyl group in **L1** was distinct and appeared as a singlet at δ 3.80 ppm (6H). (Figures S3 and S4, Supplementary Information). A characteristic ^{13}C -NMR resonance appeared at δ 157.7 and δ 156.6 which was attributed to the C2 position of the pyridyl groups for **L1** and **L2** respectively.⁴¹ Furthermore, ^{13}C -NMR signals due to the methylene– CH_2 –S– groups appeared at δ 37.35 for **L1** and δ 37.52 for **L2**. Compound **L1** also displayed a ^{13}C NMR signal for the methoxy substituents at δ 56.11 (Figures S5 and S6, Supplementary Information). Furthermore, the mass spectra of these species gave molecular ion peaks at m/z : 384.7 for **L1** and 393.8 for **L2** (Figures S1 and S2, Supplementary Information).

3.2 Synthesis and characterization of the complexes

Iron and copper complexes of the SNS pincer ligands were synthesized by direct reaction of the metal chloride with SNS ligands in methanol/THF and identified by spectral data (UV-Vis, IR and mass) and elemental analysis. In addition, the Cu complex **3** was characterized by a single crystal X-ray diffraction analysis. Many

Scheme 2. Synthesis of the pincer ligands **L1** and **L2** and their Cu(II), Fe(II) and Cu(I) complexes.

different reaction conditions were used (excess of ligand, the range of temperatures, reaction time) and in all cases the complexes with ligand-metal stoichiometry equal to 1:1 were isolated (Scheme 2). The complexes are colored, air stable, highly soluble in common organic solvents such as THF, DMF and methanol. Two new complexes have been obtained from the **L1** ligand, and these complexes are proposed to be five-coordinate $[\text{M}(\kappa^3\text{-L1})\text{Cl}_2]$ ($\text{M} = \text{Cu}$ **1** and $\text{M} = \text{Fe}$ **2**) compounds on the basis of the UV-Vis, IR, mass spectrometry (Figures S7–S10, Supplementary Information) and elemental analysis data as well as the number of reported five coordinated 2,6-bis(R-thiomethyl)pyridine complexes. The reactions with the **L2** ligand also led to the isolation of two new complexes. In the case of Fe(II), the spectroscopic and analytical data again point to a similar five-coordinate species $[\text{Fe}(\kappa^3\text{-L2})\text{Cl}_2]$ (**4**). (Figure S11, Supplementary Information). However, the complexation reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with **L2** proceeded along a different path to yield a new dimeric Cu(I) species $[\text{Cu}_2(\kappa^2\text{-L2})_2\text{Cl}_2]$ (**3**) through an apparent *in situ* reductions. Copper(II/I) reduction reactions have been reported during the formation of copper complexes in the literature.^{42,43} In our previous study it was observed that the Cu(I) complex is monomeric form.⁴² However, it was a surprise to see that the Cu(I) complex is formed in a dimeric form in this study. X-ray data in earlier research by the authors shows the structure of Cu(I) complex as a pseudo-trigonal structure.⁴² In this study, the structure of Cu(I) complex was found as a tetrahedral structure. However, this is a very rare event, so there are very few cases in the literature.

EPI mass spectra registered in methanol show peaks corresponding to the fragment $[\text{M}(\text{L})\text{Cl}_2]^+$ ($\text{M} = \text{Cu}, \text{Fe}$) for all the complexes, only **3** complex $[\text{Cu}_2(\text{L2})_2\text{Cl}_2]^+$, indicates the coordination of the pincer ligands to the metal center. Other minor signals could be assigned to $[\text{M}(\text{L})\text{Cl}_2](\text{X})^+$ units (being X the solvents such as water or THF), which could be attributed to the presence of monomeric species (Figures S7–S10, Supplementary Information). When the mass spectrum of the complex **3** is examined, it is observed that the molecular ion peak is 490.94. This likely indicates that when the complex **3** is in the solvent, the bond between the copper metals is broken into a monomeric form.

3.3 Crystal structure

Fortunately, the structures of both **L1** and $[\text{Cu}_2(\text{L2})_2\text{Cl}_2]$ copper complex (**3**) were obtained through single crystal X-ray analysis and the molecular structures and Ortep-3 views of the compounds are given in Figure 1. The crystal data for both **L1** and **3** are summarized in Table S1, Supplementary Information.

The bond length of C—N (1.337 (2) Å) has been observed as shorter than the standard C—N single bond length (1.48 Å) but it is slightly longer than standard double bond length (1.28 Å)⁴⁴ and C—O bond length observed in the range of 1.360(3)—1.423(3) Å for **L1**.

The coordination geometry of the Cu center in **3** can be described as an asymmetrical tetrahedral unit. There is also a comparison of data available with this bond for another Cu complex in the literature,^{45,46} as well as

Figure 1. X-ray structure of **L1** ligand and **3** $[\text{Cu}_2(\text{L2})_2\text{Cl}_2]$ complex.

the metal-ligand bond distances of Cu—N and Cu—S is 2.03 (4) Å and 2.40 (14) Å, respectively. It can be compared with previously published data.^{47,48} The (N1—Cu1—S2) angles of 85.6(12)° compatible with a bite angle observed but Cu—S—C angle shows different from our previous paper.⁴²

3.3a Optimized geometries: The ligands and their complexes were computationally optimized by DFT using the B3LYP functional and 6-31gd basis set. The calculated geometric parameters of ligands and their complexes are given in Table S2, Supplementary Information. The experimental structural features are well-modelled by the optimization for **L1** ligand and $[\text{Cu}_2(\text{L2})_2\text{Cl}_2]$ complex. The C—C bond lengths were around 1.36–1.51 Å for this ligand and complex. Specifically, Cu—N bond length has been obtained as 2.03 Å experimentally, and 1.97 Å has been obtained theoretically. This bond is comparable with our previous paper.⁴² The theoretical study of Cu and Fe complex of the ligand has been also performed. The S—C bond is around 1.79 Å for both Cu and Fe complex, and it has shown a similarity to each other. The bond lengths' results obtained theoretically of these complexes have shown that these structures are in harmony with each other. The experimental and computed ligand bite angles (N—Cu—S) compare well at 85.6°(12) and 85.4°, respectively. A similar bite angle (N—Fe—S, 84.9°) was obtained for the computed Fe(II) species **4**. Detailed information can be seen from Table S2, Supplementary Information.

3.3b Vibrational spectroscopy: The determination of the theoretical IR spectrum in the illumination of chemical compounds is very useful. In this study, the vibrational modes of all the synthesized compounds have been studied by comparing their experimental and

IR frequencies predicted by the DFT computations. The experimental and theoretical IR spectra of the samples investigated two ligands and four complexes (**1–4**) are given in the Supplementary Information (Table S3). Inspection of this comparison reveals that the experimental and computed data are essentially similar.

When the FT-IR spectra of the **L1** and **L2** ligands were examined, it was observed that the C=N group stretching vibration band of the pyridine ring were 1571 and 1572 cm^{-1} , respectively.^{49,50} These vibrations are observed as between 1563–1579 cm^{-1} experimentally and between 1560–1580 cm^{-1} theoretically, for all complexes.⁵¹ C=N stretching vibrations belong to the pyridine ring of ligands that shifted to lower frequencies for complex **2**, **3** and **4** and to higher frequencies for complex **1** as a result of complex formation. Dede *et al.*, expressed that these shifts occurred as a result of complexation reveals that the ligand coordinated to the metal ion through azomethine reduces electron density and bonding order of the C=N bond.^{52,53} It has been determined that the interaction of metal-N in the IR spectrum is between 570–573 cm^{-1} in the complexes.^{43,54}

3.3c HOMO–LUMO analysis: It is known that frontier orbitals play an important role in optical and electrical properties as well as their role in UV spectra and chemical reactions.⁵⁵ The energy levels and distributions of the HOMO and LUMO orbitals, obtained from a DFT computation with the B3LYP functional and 6-31G (d) basis set for the title compounds, are shown in Figure 2 and Figure S12, Supplementary Information. The gap between HOMO and LUMO characterizes molecular chemical stability.⁵⁶ The excited probability of electrons decreases with the increase in HOMO–LUMO energy number. As a result of calculations, the energy ranges between HOMO and LUMO orbitals of **L1**, **3**, **1**, **2** and **4** studied molecules were

Figure 2. The energy levels and distributions of the HOMO and LUMO orbitals of L1 ligand and its complexes.

found to be 0.17045, 0.10556, (Alpha = 0.49886 and Beta = 0.11457), 0.11626 and 0.11684 eV, respectively. According to this result, the excitation probability of the electrons when it has copper structures is lower than that of the electrons in the ferrous and metal-free structures.

3.3d Molecular electrostatic potential: Molecular electrostatic potential (MEP) known as the interaction between the unit positive charge and the molecular charge distribution of the system plays an important role in the determination of intermolecular interactions and chemical reactions.^{57,58} The DFT optimizations provide the electron distributions for ligands and complexes. The

most negative (electron density) region in the map given in Figure 3 (L1, 1, 2) and Figure S13 (Supplementary Information) are shown in red. It is between the S1 and O1 atoms and the value -0.0377 a.u. for L1. Perhaps not too surprisingly, the highest electron density found for the metal complexes here is the chloro ligands and this extends to include the 'pocket' formed by the chelating S centers. The most electron poor/positive region, are shown in blue on maps and are on the periphery of the complexes. Here, the intermediate values are represented by other colors on this scale.^{59–61} The MEP surface and 2D contour maps drawn in the molecular plane clearly suggest the different values of electrostatic potential in the molecule.

Figure 3. The MEP surface and 2D contour maps of L1 ligand and its complexes.

Table 1. The results of the cycloaddition reaction of ECH with CO₂ catalyzed by SNS type metal complexes.

Entry	Cat.	Yield ^a (%)	Selectivity ^a (%)	TON ^b	TOF ^c (h ⁻¹)
1	1	78.2	99.4	782	391
2	2	89.9	98.9	899	450
3	3	71.9	99.2	719	360
4	4	87.7	98.9	877	439
5	— ^d	5.0	99.0	50	25
6	2 ^e	3.8	78.3	380	190

Reaction conditions: Cat. (4.5×10^{-5} mol), epichlorohydrin (4.5×10^{-2} mol), DMAP (9×10^{-5} mol), CO₂ (1.6 MPa), 100 °C, 2 h.

^aYield and selectivity of epoxide to corresponding cyclic carbonate were determined by GC.

^bMoles of cyclic carbonate produced per mole of catalyst.

^cThe rates expressed in terms of the turnover frequency {TOF [mol of product (mol of catalyst h)⁻¹] = turnovers/h}

^dBlank Run with no added Cat., DMAP = 9×10^{-5} mol.

^ethe reaction was carried out using **2** alone

3.4 Catalytic studies

Given that one of our broad interest is in using CO₂ as a chemical feedstock and in exploring atom-economical processes, the application of these new SNS ligand complexes in the synthesis of 4-(chloromethyl)-1,3-dioxolan-2-one (ECHC) synthesis from epichlorohydrin (ECH) and CO₂ is explored. The initial catalytic experiments started with reaction conditions that were

used in earlier studies by this research's authors.^{62–65}

In the presence of the four SNS complexes **1–4**, the coupling reactions of ECH and CO₂ to form ECHC were carried out under identical reaction conditions (0.1% catalyst loading, 0.2% 4-dimethylamino pyridine (DMAP), CO₂ pressure = 1.6 MPa, 100 °C for 2 h) and the corresponding results are summarized in Table 1. All four of the complexes (**1–4**) prepared in this study, when used with a co-catalyst, showed high catalytic activity

Figure 4. Cycloaddition of CO₂ to different epoxides catalyzed by the **2**.

and selectivity for the conversion of CO₂ and ECH into ECHC. When the reaction was carried out using **2** alone, the ECHC yield was only 3.8%, while the sole DMAP gave a 5% yield, and surprisingly, the combination of **2** and DMAP in the same reaction condition provided 89.9% yield of the desired ECHC, indicating certain synergetic catalysis occurring between **2** and DMAP, but neither **2** nor DMAP could catalyse in such a high reaction yield separately (Table 1, entry 2, 5–6). The highest activity with an 89.9% yield was observed with Fe complex **2** as catalyst (Table 1, entry 2). Curiously, the complexes of the **L1** ligand gave higher yields in proportion to those with the **L2** ligand (Table 1, entry 1–4). Furthermore, the complexes of the Fe(II) metal gave higher yields compared to those with the Cu(II) metal as similar results were reported previously by the authors.⁴² The **2**, when using DMAP as the co-catalyst, showed the best catalytic performance (89.9% yield and 98.9% selectivity) with ECH as a substrate within 2 h, with CO₂ pressure 1.6 MPa at 100 °C (Table 1).

3.4a Effect of reaction parameters (epoxide, temperature, CO₂ pressure and time) on the cycloaddition reaction: In order to investigate the substrate content for this reaction, the addition of CO₂ to different epoxides was examined using 0.1 mol% of complex **2** as the best active catalyst, 0.2% DMAP as co-catalyst, and 1.6 MPa of CO₂ at 100 °C. Five different epoxides, propylene oxide (PO), 1,2-epoxybutane (EB), epichlorohydrin (ECH), styrene oxide (SO) and cyclohexene oxide (CHO) were used as both solvent and substrate under the optimized reaction conditions and the results of this study are shown in Figure 4. The ECH was found to be the most reactive epoxide, while cyclohexene oxide (CHO) exhibited the lowest activity of the epoxides surveyed. This result may be due to more electrons donating substituents linked to C2-atom of

these epoxides (SO, PO, EB, and CHO) which could be coordinately bonded to the metal center and was responsible for the catalyst poisoning.⁶⁵ CHO showed the lowest activity, which might be due to the high steric hindrance caused by the cyclohexene ring.⁶⁶ There are similar reactivity studies in the literature.^{62,63,67–69}

The effects of temperature, CO₂ pressure and reaction time on the catalytic performance of **2** for the formation of ECHC from ECH and CO₂ were investigated. The transformation of CO₂ to ECHC using **2**/DMAP as a catalyst was investigated as a model reaction system (Figures S14–S16, Supplementary Information). The results in Figure S14 (Supplementary Information) clearly show that the catalytic activity of **2** was sensitive to the reaction temperature of the CO₂ coupling reaction. Just a 58.1% yield of ECHC was obtained at 75 °C and this yield increased to 97.5% at 125 °C. The yield and selectivity of ECHC increased with the reaction temperature up to 125 °C, whereas any further increase in temperature caused a decrease in the selectivity and catalytic activity, possibly due to the decomposition of the product into side-products formed at the higher temperature, such as 1-chloroethane-1,2-diol.⁷⁰

The influence of CO₂ pressure showed on the ECHC yield and selectivity. Catalytic reactions were conducted at 0.5, 1, 1.6, 2.5 and 4 MPa CO₂ pressure. As shown in Figure S15 (Supplementary Information), in the low-pressure range (0.5–1.6 MPa), the yield of ECHC increased from 86.2% to 97.5% when compared to the initial CO₂ pressure of 0.5 MPa, but a further rise of pressure to 4 MPa resulted in a slight decrease of catalytic yield (from 97.5% to 95.9%). A further increase in CO₂ pressure caused a slight decrease of ECHC yield as well as a slight decrease in selectivity because the concentration of ECH decreased, along with an increased amount of dissolved CO₂ at higher pressure. This indicates that 1.6 MPa is the optimal CO₂ pressure for the

transformation of CO₂ to ECHC using **2**/DMAP. Similar influences of CO₂ pressure on catalytic results were observed in our previous studies and by others.^{62–65,67–69,71,72}

The effect of reaction times on the yield and selectivity for ECHC formation catalyzed by **2** is shown in Figure S16, Supplementary Information. The cycloaddition reaction proceeds quickly and almost completes within the first 2 h, reaching an ECHC yield of 97.5%. By Prolonging the reaction time from 0.5 to 4 h, ECHC yield increased from 95.2 to 98.5% with CO₂ pressure of 1.6 MPa at 100 °C (Figure S16, Supplementary Information). In order to optimize the time investment in this transformation, a reaction time of 2 h as the optimal option for the conversion of CO₂ was chosen to be employed.

4. Conclusions

This report describes some first-row transition metal complexes supported by sterically demanding SNS pin-cer type ligands. Two new ligands and their Cu and Fe complexes have been experimentally characterized using various characterization techniques. Complexes **1**, **2** and **4** have five coordinated structures, while complex **3** has surprisingly tetrahedral geometry. The structure of the complex **3** was confirmed as a tetrahedral geometry by single crystal X-ray diffraction analysis. The effectiveness of these four newly synthesized SNS complexes as catalysts in obtaining cyclic carbonates from the reactions of epoxides with CO₂ has been investigated. The Fe(κ^3 -**L1**)Cl₂ complex **2** was found to be a slightly more active catalyst than the other complexes. The effect of temperature and CO₂ pressure on this transformation was investigated and the scope was shown by reporting the ability to use five different epoxides in this reaction. The structures of the complexes without crystal forms were supported by DFT studies. The experimental results are in agreement with the theoretical results.

Supplementary Information (SI)

Crystallographic data for the structures reported in this article were deposited in the Cambridge Structural Database as supplementary publication number CCDC 1568427 and 1568428 for C₂₁H₂₁N₁O₂S₂ ligand and C₃₈H₃₀Cl₆Cu₂N₂S₄ complex, respectively. Copies of the data can be obtained free of charge on application to CCDC 12 Union Road, Cambridge CB21 EZ, UK. (Fax: (+44) 1223 336-033; e-mail: data_request@ccdc.cam.ac.uk). All additional information pertaining to characterization of the **L1** ligand and [Cu₂(κ^2 -**L2**)₂Cl₂] complex using X-ray CIF, Mass (Figures S1, S2, S7–S10) and NMR (Figures S3, S4, S5 and

S6), Molecular structure (Figure S11), the energy levels and distributions of the HOMO and LUMO orbitals of **3** and **4** complexes (Figure S12), the MEP surface and 2D contour maps of **3** and **4** complexes (Figure S13), Influence of reaction temperature on ECHC yield and selectivity catalyzed by the **2** (Figure S14), Influence of reaction pressure on ECHC yield and selectivity catalyzed by the **2** (Figure S15), Influence of reaction time on ECHC yield and selectivity catalyzed by the **2** (Figure S16), selected optimized and crystallographic data for **L1** and **3** (**Cu**) compounds (Table S1) and experimental geometries parameters of **L1** ligand and **3** (**Cu**) compounds in ground state (Table S2) and comparison of the experimental and calculated vibrational frequencies (cm⁻¹) (Table S3) are given in the supporting information available at www.ias.ac.in/chemsci.

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References

1. Karam A R, Catari E L, Lopez-Linares F, Agrifoglio G, Albano C L, Diaz-Barrios A, Lehmann T E, Pekerar S V, Albornoz L A, Atencio R, Gonzalez T, Ortega H B and Joskowics P 2005 Synthesis, characterization and olefin polymerization studies of iron(II) and cobalt(II) catalysts bearing 2,6-bis(pyrazol-1-yl)pyridines and 2,6-bis(pyrazol-1-ylmethyl)pyridines ligands *Appl. Catal. A: Gen.* **280** 165
2. Martin E and Dieguez M 2007 Thioether containing ligands for asymmetric allylic substitution reactions *C. R. Chimie* **10** 188
3. Annaraj J, Kim S, Seo M S, Lee Y-M, Kim Y, Kim S-J, Choi Y S, Jang H G and Nam W 2009 An iron(II) complex with a N₃S₂ thioether ligand in the generation of an iron(IV)-oxo complex and its reactivity in olefin epoxidation *Inorg. Chim. Acta* **362** 1031
4. Fernandes R R, Lasri J, da Silva M F C G, da Silva J A L, da Silva J J R F and Pombeiro A J L 2011 Bis- and tris-pyridyl amino and imino thioether Cu and Fe complexes. Thermal and microwave-assisted peroxidative oxidations of 1-phenylethanol and cyclohexane in the presence of various N-based additives *J. Mol. Catal. A: Chem.* **351** 100
5. Balamurugan R, Palaniandavar M and Gopalan R S 2001 Trigonal planar copper(I) complex: Synthesis, structure, and spectra of a redox pair of novel copper(II/I) complexes of tridentate bis(benzimidazol-2'-yl) ligand framework as models for electron-transfer copper proteins *Inorg. Chem.* **40** 2246
6. Balamurugan R, Palaniandavar M, Gopalan R S and Kulkarni G U 2004 Copper(II) complexes of new pentadentate bis(benzimidazolyl)-dithioether ligands: Synthesis, structure, spectra and redox properties *Inorg. Chim. Acta* **357** 919
7. Whelan J and Bosnich B 1986 Biological analogs. A structural model for the binding site of blue copper proteins *Inorg. Chem.* **25** 3671

8. Miecznikowski J R, Lynn M A, Jasinski J P, Lo W, Bak D W, Pati M, Butrick E E, Drozdowski A E R, Archer K A, Villa C E, Lemons E G, Powers E, Siu M, Gomes C D, Bernier N A and Morio K N 2014 Synthesis and characterization of five-coordinate copper(II) complexes based on tridentate SNS pincer ligand precursors *Polyhedron* **80** 157
9. Solomon E I, Szilagyi R K, George S D and Basumallick L 2004 Electronic structures of metal sites in proteins and models: Contributions to function in blue copper proteins *Chem. Rev.* **104** 419
10. Holland P L and Tolman W B 1999 Three-coordinate Cu(II) complexes: Structural models of trigonal-planar type I copper protein active sites *J. Am. Chem. Soc.* **121** 7270
11. Holland P L and Tolman W B 2000 A structural model of the type I copper protein active site: N₂S(thiolate)S(thioether) ligation in a Cu(II) complex *J. Am. Chem. Soc.* **122** 6331
12. Balamurugan R, Palaniandavar M, Stoeckli-Evans H and Neuburger M 2006 Axial versus equatorial coordination of thioether sulfur: Mixed ligand copper(II) complexes of 2-pyridyl-N-(20-methylthiophenyl)-methyleneimine with bidentate diimine ligands *Inorg. Chim. Acta* **359** 1103
13. Nekola H and Rehder D 2002 A penta-coordinated zinc complex containing a bio-mimetic NS₂S'₂ (thiolate/thioether) ligand *Inorg. Chim. Acta* **337** 467
14. Barth J V 2007 Molecular Architectonic on Metal Surfaces *Annu. Rev. Phys. Chem.* **58** 375
15. Ma Z and Zera F 2006 Organic chemistry on solid surfaces *Surf. Sci. Rep.* **61** 229
16. Pan Y, Nilus N, Schneider W D and Freund H J 2014 Adsorption of thioether molecules on an alumina thin film *Surf. Sci.* **628** 111
17. Werner T and Tenhumberg N 2014 Synthesis of cyclic carbonates from epoxides and CO₂ catalyzed by potassium iodide and amino alcohols *J. CO₂ Utilization* **7** 39
18. Aresta M and Dibenedetto A 2007 Utilisation of CO₂ as a chemical feedstock: opportunities and challenges *Dalton Trans.* 2975
19. Mikkelsen M, Jorgensen M and Krebs F C 2010 The teraton challenge. A review of fixation and transformation of carbon dioxide *Energ. Environ. Sci.* **3** 43
20. Darensbourg D J and Holtcamp M W 1996 Catalysts for the reactions of epoxides and carbon dioxide *Coord. Chem. Rev.* **153** 155
21. Sakakura T and Kohno K 2009 The synthesis of organic carbonates from carbon dioxide *Chem. Commun.* **11** 1312
22. Dai W L, Luo S L, Yin S F and Au C T 2009 The direct transformation of carbon dioxide to organic carbonates over heterogeneous catalysts *Appl. Catal. A: Gen.* **366** 2
23. Omae I 2012 Recent developments in carbon dioxide utilization for the production of organic chemicals *Coord. Chem. Rev.* **256** 1384
24. Muthuramalingam S, Velusamy M and Mayilmurugan R 2018 Fixation and sequestration of carbon dioxide by copper(II) complexes *J. Chem. Sci.* **130** 78
25. Shaikh A A G and Sivaram S 1996 Organic Carbonates *Chem. Rev.* **96** 951
26. Stamp L M, Mang S A, Holmes A B, Kinghts K A, de Miguel Y R and McConvey I F 2001 Polymer supported chromium porphyrin as catalyst for polycarbonate formation in supercritical carbon dioxide *Chem. Commun.* 2502
27. Paddock R L and Nguyen S T 2001 Chemical CO₂ fixation: Cr(III) salen complexes as highly efficient catalysts for the coupling of CO₂ and epoxides *J. Am. Chem. Soc.* **123** 11498
28. Paddock R L, Hiyama Y, McKay J M and Nguyen S T 2004 Co(III) porphyrin/DMAP: An efficient catalyst system for the synthesis of cyclic carbonates from CO₂ and epoxides *Tetrahedron Lett.* **45** 2023
29. Barbarini A, Maggi R, Mazzacani A, Mori G, Sartori G and Sartori R 2003 Cycloaddition of CO₂ to epoxides over both homogeneous and silica-supported guanidine catalysts *Tetrahedron Lett.* **44** 2931
30. Ramin M, Grunwaldt J D and Baiker 2005 A Behavior of homogeneous and immobilized zinc-based catalysts in cycloaddition of CO₂ to propylene oxide *J. Catal.* **234** 256
31. Dorskocil E J, Bordawekar S V, Kaye B C and Davis R J 1999 UV-Vis spectroscopy of iodine adsorbed on alkali-metal-modified zeolite catalysts for addition of carbon dioxide to ethylene oxide *J. Phys. Chem. B* **103** 6277
32. Bhanage B M, Fujita S, Ikushima Y and Arai M 2001 Synthesis of dimethyl carbonate and glycols from carbon dioxide, epoxides, and methanol using heterogeneous basic metal oxide catalysts with high activity and selectivity *Appl. Catal. A: Gen.* **219** 259
33. Wang J Q, Yue X D, Cai F and He L N 2007 Solventless synthesis of cyclic carbonates from carbon dioxide and epoxides catalyzed by silica-supported ionic liquids under supercritical conditions *Catal. Commun.* **8** 167
34. Agilent, CrysAlis PRO, Agilent Technologies, Yarnton, Oxfordshire, England, 2012
35. Dolomanov O V, Bourhis L J, Gildea R J, Howard J A K and Puschmann H J 2009 OLEX2: A complete structure solution, refinement and analysis program *J. Appl. Cryst.* **42** 339
36. Sheldrick G M 2015 SHELXT – Integrated space-group and crystal-structure determination *Acta Cryst. A* **71** 3
37. Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Mennucci B, Petersson G A, Nakatsuji H, Caricato M, Li X, Hratchian H P, Izmaylov A F, Bloino J, Zheng G, Sonnenberg J L, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery Jr. J A, Peralta J E, Ogliaro F, Bearpark M, Heyd J J, Brothers E, Kudin K N, Staroverov V N, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant J C, Iyengar S S, Tomasi J, Cossi M, Rega N, Millam J M, Klene M, Knox J E, Cross J B, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Martin R L, Morokuma K, Zakrzewski V G, Voth G A, Salvador P, Dannenberg J J, Dapprich S, Daniels A D, Farkas O, Foresman J B, Ortiz J V, Cioslowski J, Fox D J, Gaussian 09, Revision C.1, Gaussian Inc., Wallingford, CT, 2009
38. Becke A D 1993 Density-functional thermochemistry. III. The role of exact exchange *J. Chem. Phys.* **98** 5648

39. Lee C, Yang W and Parr R G 1988 Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density *Phys. Rev. B* **37** 785
40. Dennington R, Keith T and Millam J 2009 GaussView, Version 5, Semichem Inc., Shawnee Mission, KS
41. Tümer M, Deligonül N, Gölcü A, Akgün E, Dolaz M, Demirelli H and Dıǧrak M 2006 Mixed-ligand copper(II) complexes: investigation of their spectroscopic, catalysis, antimicrobial and potentiometric properties *Trans. Met. Chem.* **31** 1
42. Sogukomerogullari H G, Aytar E, Ulusoy M, Demir S, Dege N, Richeson D S and Sönmez M 2018 Synthesis of complexes Fe, Co and Cu supported by “SNS” pincer ligands and their ability to catalytically form cyclic carbonates *Inorg. Chim. Acta* **471** 290
43. Miecznikowski J R, Lynn M A, Jasinski J P, Reinheimer E, Bak D W, Pati M, Butrick E E, Drozdowski A E R, Archer K A, Villa C E, Lemons E G, Powers E, Siu M, Gomes C D and Morio K N 2014 Synthesis, characterization, and computational study of three-coordinate SNS-copper(I) complexes based on bis-thione precursors *J. Coord. Chem.* **67** 29
44. Sarioğlu A O, Ceylan Ü, Yalçın Ş P, Sönmez M, Ceyhan G and Aygün M 2016 Synthesis of a new ONNO donor tetradentate schiff base ligand and binuclear Cu(II) complex: Quantum chemical, spectroscopic and photoluminescence investigations *J. Lumin.* **176** 193
45. Sasmal A, Shit S, Rizzoli C, Wang H, Desplanches C and Mitra S 2012 Framework solids based on copper(II) halides (Cl/Br) and methylene-bridged bis(1-hydroxybenzotriazole): Synthesis, crystal structures, magneto-structural correlation, and density functional theory (DFT) studies *Inorg. Chem.* **51** 10148
46. Espinoza S, Arce P, San-Martín E, Lemus L, Costamagna J, Farías L, Rossi M, Caruso F and Guerrero J 2015 The crystal structure of mono- and di-nuclear copper(I) complexes with substituted triphenylphosphine ligands *Polyhedron* **85** 405
47. Nielsen A, Veltze S, Bond A D and McKenzie C J 2007 Isomerism in copper(II) chloride complexes of bis(2-pyridylmethyl)amine and N-substituted derivatives: Synthesis and X-ray structural characterization *Polyhedron* **26** 1649
48. Gu S, Du J, Huang J, Xi H, Yang L, Xu W and Lu C 2016 Bi- and trinuclear copper(I) complexes of 1,2,3-triazole-tethered NHC ligands: Synthesis, structure, and catalytic properties *Beilstein J. Org. Chem.* **12** 863
49. Wong K N and Colson S D 1984 The FT-IR spectra of pyridine and pyridine- d_5^1 *J. Mol. Spectrosc.* **104** 129
50. Sogukomerogullari H G, Şen F, Dinçer M, Özdemir N and Sönmez M 2017 Tridentate SNS pincer type ligand: Synthesis, structural and spectroscopic analysis of a novel pyridine and m-xylene compound with thioether-bridge *J. Mol. Struct.* **1136** 271
51. Vaughan T F and Spencer J L 2016 Synthesis, properties and group 10 metal complexes of a bis(dipyridylphosphinomethyl)phenyl pincer ligand *Inorg. Chim. Acta* **442** 24
52. Dede B, Özen N and Görgülü G 2018 Synthesis, characterization, theoretical calculations and enzymatic activities of novel diimine-dioxime ligand and its homodinuclear Cu(II) complex *J. Mol. Struct.* **1163** 357
53. Jafari-Moghaddam F, Beyramabadi S A, Khashi M and Morsali A 2018 Three VO²⁺ complexes of the pyridoxal-derived Schiff bases: Synthesis, experimental and theoretical characterizations, and catalytic activity in a cyclocondensation reaction *J. Mol. Struct.* **1153** 149
54. Zhang J, Pan M, Jiang J, She Z, Fan Z and Su C 2011 Syntheses, crystal structures and antimicrobial activities of thioether ligands containing quinoline and pyridine terminal groups and their transition metal complexes *Inorg. Chim. Acta* **374** 269
55. Fleming I 1976 *Frontier Orbitals and Organic Chemical Reactions* (London: Wiley)
56. Fukui K 1982 Role of Frontier Orbitals in Chemical Reactions *Science* **218** 747
57. Arslan N B, Kazak C and Aydın F 2018 Experimental and theoretical investigation of N-(4-nitrobenzoyl)-S-(cyclohexyl)-dithiocarbamate, N-(4-nitrobenzoyl)-S-benzyl di thiocarbamate *J. Mol. Struct.* **1155** 646
58. Büyüksulu H, Akdoğan M, Yıldırım G and Parlak C 2010 Ab initio Hartree-Fock and density functional theory study on characterization of 3-(5-methylthiazol-2-ylidiazetyl)-2-phenyl-1H-indole *Spectrochim. Acta Part A* **75** 1362
59. Eşme A and Sağdıç S G 2017 Spectroscopic (FT-IR, FT-Raman, UV-Vis) analysis, conformational, HOMO-LUMO, NBO and NLO calculations on monomeric and dimeric structures of 4-pyridazinecarboxylic acid by HF and DFT methods *J. Mol. Struct.* **1147** 322
60. Durgun M, Ceylan Ü, Yalçın Ş P, Türkmen H, Özdemir N and Koyuncu İ 2016 Synthesis, molecular structure, spectroscopic characterization, NBO, NLO and NPA analysis and in vitro cytotoxicity study of 3-chloro-N-(4-sulfamoylphenethyl)propanamide with experimental and computational study *J. Mol. Struct.* **1114** 95
61. Gökce H, Öztürk N, Ceylan Ü, Alpaslan Y B and Alpaslan G 2016 Thiol–thione tautomeric analysis, spectroscopic (FT-IR, Laser-Raman, NMR and UV-vis) properties and DFT computations of 5-(3-pyridyl)-4H-1,2,4-triazole-3-thiol molecule *Spectrochim. Spectrochim. Acta Part A* **163** 170
62. Kilic A, Kilic M V, Ulusoy M, Durgun M, Aytar E, Dagdevren M and Yılmaz I 2014 Ketone synthesized cobaloxime/organocobaloxime catalyst for functional cyclic carbonate synthesis from CO₂ and epoxides: Characterization and electrochemistry *J. Organomet. Chem.* **767** 150
63. Kilic A, Ulusoy M, Durgun M, Aytar E, Keles A, Dagdevren M and Yılmaz I 2014 The cycloaddition of carbon dioxide and epoxides catalyzed by molecular cobaloximes: Synthesis, characterization and electrochemistry *J. Coord. Chem.* **67** 2661
64. Kilic A, M Ulusoy, Durgun M and Aytar E 2014 The multinuclear cobaloxime complexes-based catalysts for direct synthesis of cyclic carbonate from of epichlorohydrin using carbon dioxide: Synthesis and characterization *Inorg. Chim. Acta* **411** 17
65. Ulusoy M, Cetinkaya E and Cetinkaya B 2009 Conversion of carbon dioxide to cyclic carbonates using diimine Ru(II) complexes as catalysts *Appl. Organomet. Chem.* **23** 68

66. Zhu A, Jiang T, Han B, Zhang J, Xie Y and Ma X 2007 Supported choline chloride/urea as a heterogeneous catalyst for chemical fixation of carbon dioxide to cyclic carbonates *Green Chem.* **9** 169
67. Kilic A, Ulusoy M, Durgun M, Tasci Z, Yilmaz I and Cetinkaya B 2010 Hetero- and homo-leptic Ru(II) catalyzed synthesis of cyclic carbonates from CO₂; Synthesis, spectroscopic characterization and electrochemical properties *Appl. Organomet. Chem.* **24** 446
68. Ulusoy M, Kilic A, Durgun M, Tasci Z and Cetinkaya B 2011 Silicon containing new salicylaldehyde Pd(II) and Co(II) metal complexes as efficient catalysts in transformation of carbon dioxide (CO₂) to cyclic carbonates *J. Organomet. Chem.* **696** 1372
69. Kilic A, Durgun M, Aytar E and Yavuz R 2018 Synthesis and characterization of novel positively charged organocobaloximes as catalysts for the fixation of CO₂ to cyclic carbonates *J. Organomet. Chem.* **858** 78
70. Xiao L F, Yue Q F, Xia C G and Xu L W 2008 Supported basic ionic liquid: Highly effective catalyst for the synthesis of 1,2-propylene glycol from hydrolysis of propylene carbonate *J. Mol. Catal. A: Chem.* **279** 230
71. Xie Y, Zhang Z, Jiang T, He J, Han B, Wu T and Ding K 2007 CO₂ Cycloaddition reactions catalyzed by an ionic liquid grafted onto a highly cross-linked polymer matrix *Angew. Chemie - Int. Ed.* **46** 7255
72. Darensbourg D J, Mackiewicz R M and Billodeaux D R 2005 Pressure dependence of the carbon dioxide/cyclohexene oxide coupling reaction catalyzed by chromium salen complexes. Optimization of the comonomer-alternating enchainment pathway *Organomet.* **24** 144