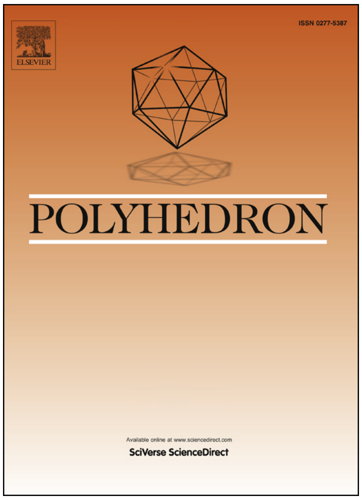

Solvomorphism and catecholase activities of bis(μ-phenoxido)dicopper(II) complexes

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Solvomorphism and catecholase activities of bis(μ-phenoxido)dicopper(II) complexes

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Abstract

Two phenoxido bridged dinuclear Cu(II) complexes, $[Cu_2(L^1)_2(NCO)_2]$ (**1**), and $[Cu_2(L^2)_2(NCO)_2]\cdot 2CH_3OH$ (**2**) have been synthesized using the tridentate reduced Schiff-base ligands 2-[(2-dimethylamino-ethylamino)-methyl]-phenol (HL^1) and 2-[(2-diethylamino-ethylamino)-methyl]-phenol (HL^2) respectively. Re-crystallization of compound **2** from dichloromethane produced desolvated complex $[Cu_2(L^2)_2(NCO)_2]$ (**3**). The compounds **2** and **3** are pseudopolymorphs or solvomorphs which differ in the inclusion of methanol molecules and in the crystal system (orthorhombic, *P*bca for **2** and monoclinic, $P2_1/n$ for **3**). The complexes have been characterized by X-ray structural analyses and spectroscopic methods. In all three complexes Cu(II) is penta-coordinated having the geometry intermediate between distorted square pyramid and trigonal bipyramid with Addison parameter (τ) = 0.33, 0.48 and 0.53 for **1, 2** and **3** respectively. Using 3,5-di-*tert*-butylcatechol (3,5-DTBC) as the substrate, the catecholase activity of complexes **1** and **2** has been studied in methanol solution; compound **2** shows slightly higher catecholase activity ($k_{cat} = 98.4\ h^{-1}$) than compound **1** ($k_{cat} = 64.2\ h^{-1}$).

Keywords: Copper(II); Reduced Schiff base; Crystal structure; Solvomorphs, Catecholase activity.

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1. Introduction

The oxidation of organic substrates with molecular oxygen under mild conditions is of great interest for industrial and synthetic processes both from an economical and environmental point of view [1]. The synthesis and investigation of functional model complexes for metalloenzymes with oxidase or oxygenase activity is therefore of great promise for the development of new and efficient catalysts for oxidation reactions. Catechol oxidase is a type III active site protein containing copper which catalyzes the oxidation of a wide range of o-diphenols (catechols) to the corresponding o-quinones in a process known as catecholase activity [2]. The ability of dicopper complexes to oxidize phenols and catechols is well known. The extensive studies performed with copper-based model complexes have shown that various structural factors may affect their catalytic activity, namely the metal-metal distance, type of exogenous bridging ligand, coordination geometry around the metal ion, and flexibility of the ligand [3-12]. In the dinuclear complexes, a copper-copper distance of 2.9-3.2 Å has been suggested as providing maximum catecholase activity owing to the requirement of a steric match between the substrate and the catalyst [13]. Various type of ligands are used to obtain dinuclear Cu(II) complexes. Among them, the tridentate N,N,O donor Schiff bases, derived from diamines and salicylaldehyde derivatives have been used extensively [14-17]. The reduced Schiff-base ligands have been gaining popularity over the last few years, as a result of their higher stability and increased flexibility (imparted by –CH_2–NH– moieties) compared to that of the corresponding Schiff bases which include rigid azomethine (–CH=N–) fragments [7,18-26]. These tridentate N,N,O donors reduced Schiff bases are also found to generate dinuclear copper(II) complexes similar to the corresponding unreduced Schiff bases but with diferent amount of distortion around the Cu(II) centre. Such differences play an important role in catecholase activity of the complexes and therefore we would like to synthesise new dinuclear Cu(II) complexes using reduced Schiff base ligands.

During the course of this study, we are able to grow pseudopolymorphs. Pseudopolymorphism or solvomorphism is the phenomenon wherein a compound is obtained in crystalline forms that differ in the nature or stoichiometry of included solvent molecules [27-29] and are particularly important in the pharmaceutical industry where control over properties such as solubility, bioavailability and stability of the active drug is desirable [30-33]. It has been found from the literature that the introduction of solvent molecules in the molecular crystals give rise to a solvated crystals (pseudopolymorphic forms), which often have different structures compared to the structures of host crystals (devoid of solvent molecules), provides a way of perturbing the intermolecular interactions and hence the reactivity of molecules in the solid state [32].

In this paper we report the syntheses, crystal structures, and catecholase activities of two phenoxido bridged dinuclear Cu(II) complexes, $[Cu_2(L^1)_2(NCO)_2]$ (**1**), $[Cu_2(L^2)_2(NCO)_2]\cdot 2CH_3OH$ (**2**), obtained from the reduced Schiff base ligands 2-[(2-dimethylamino-ethylamino)-methyl]-phenol (HL^1) and 2-[(2-diethylamino-ethylamino)-methyl]-

phenol (HL^2) respectively. The re-crystalisation of compound **2** from dichloromethane produced the complex $[Cu_2(L^2)_2(NCO)_2]$ (**3**). The compounds **2** and **3** are solvomorphs.

2. Experimental

The reagents and solvents used were of commercially available reagent quality.

2.1. Synthesis of the reduced Schiff base ligands ((HL^1) 2-[(2-dimethylamino-ethylamino)-methyl]-phenol and (HL^2) 2-[(2-diethylamino-ethylamino)-methyl]-phenol

The Schiff base ligand was synthesized by refluxing a solution of salicylaldehyde (0.52 mL, 5 mmol) and N,N-dimethylethylenediamine (0.54 mL, 5 mmol) in methanol (30 mL) for one hour [34]. The solution was cooled to 0ºC and solid sodium borohydride (210 mg, 6 mmol) was added slowly to this methanolic solution with stirring. After completion of the addition, the resulting solution was acidified with concentrated HCl (5 ml) and then evaporated to dryness. The reduced Schiff base ligand HL^1 was extracted from the solid mass with methanol and this methanol solution (ca. 20 mL) was used for preparation of complexes. HL^2 was synthesized in the same way as HL^1 using N,N-diethylethylenediamine (0.70 mL, 5 mmol) instead of N,N-dimethylethylenediamine [12].

*2.2 Synthesis of the complexes $[Cu_2(L^1)_2(NCO)_2]$ (**1**), $[Cu_2(L^2)_2(NCO)_2]\cdot 2CH_3OH$ (**2**), and $[Cu_2(L^2)_2(NCO)_2]$ (**3**)*

An extracted methanol solution of HL^1 as prepared above was added to a solution of $CuCl_2\cdot 2H_2O$ (0.850 g, 5.00 mmol) in methanol (20 mL) and an aqueous solution (1 mL) of sodium cyanate (0.325 g, 5.00 mmol) was added to this mixture with stirring. The mixture was stirred for 1 h and filtered. The filtrate was kept undisturbed at room temperature. Green crystals of **1** suitable for X-ray diffraction were obtained after 3 days on slow evaporation of the solvent. The green crystals of complex **2** was obtained in the same way by using HL^2 instead of HL^1. The re-cystalisation of compound **2** (1 mmol) from dichloromethane produced compound **3**.

Complex 1: (Yield: 1.090 g; 73%) *Anal.* Calc. for $C_{26}H_{38}Cu_2N_6O_4$: C, 49.91; H, 6.12; N, 13.43 %. Found: C, 49.65; H, 6.05; N, 13.09 %. λmax (nm), [ε_{max} (dm^3 mol^{-1} cm^{-1})] (metanol), 650(317), 415(1523); IR: ν(N–H), 3220 cm^{-1}, ν(C–N),1596 cm^{-1} ,

Complex 2: (Yield: 1.418 g, 79 %), *Anal.* calc. for $C_{30}H_{50}Cu_2N_6O_6$: C, 50.19; H, 7.02; N, 11.71 %. found: C, 49.87; H, 6.75; N, 11.47 %. IR (KBr): ν(N–H), 3217 cm^{-1}, ν(C–N), 1596 cm^{-1}; λmax (nm), [ε_{max} (dm^3 mol^{-1} cm^{-1})] (methanol), 622 (618), 425 (1588).

Complex 3: (Yield: 0.523 g, 80 %), *Anal.* calc. for $C_{28}H_{42}Cu_2N_6O_4$: C, 51.44; H, 6.48; N, 12.85 %. found: C, 51.12; H, 6.23; N, 12.62 %. IR (KBr): ν(N–H), 3201 cm^{-1}, ν(C–N), 1595 cm^{-1}; λmax (nm), [ε_{max} (dm^3 mol^{-1} cm^{-1})] (methanol), 622 (618), 425 (1588).

2.3. Catalytic oxidation of 3,5-DTBC

In order to study the catecholase activity of the complexes, 10^{-4} (M) solutions of **1** and **2** in methanol were treated with 100 equivalents of 3,5-di-*tert*-butylcatechol (3,5-DTBC) in methanol under aerobic condition at room temperature. Absorbance vs. wavelength (wavelength scan) of these solutions was recorded at a regular time interval of 10 min in the wavelength range 300-600 nm. To determine the dependence of rate on substrate concentration and various kinetic parameters, a 10^{-4} (M) solution of complexes was treated with 10, 30, 50, 70, and 100 equivalents of substrate. The reactions were followed spectrophotometrically by monitoring the increase in the absorbance at 390 nm (quinone band maxima) as a function of time (time scan).

2.4. Physical Measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra in KBr (4500-500 cm^{-1}) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra in methanol (1200-350 nm) were recorded in a Hitachi U-3501 spectrophotometer. Thermal analysis (TG-DTA) were carried out on a Mettler Toledo TGA/SDTA 851 thermal analyzer in a dynamic atmosphere of dinitrogen (flow rate = 30 cm^3 min^{-1}). The samples were heated in an alumina crucible at a rate of 5 °C min^{-1}. Electrochemical studies were done using PAR 273 potentiostat. The measurements were performed at 300 K in acetonitrile solutions containing 0.2 M TEAP and 10^{-3} M complex deoxygenated by bubbling with nitrogen. The working, counter, and reference electrodes used were a platinum wire, a platinum coil, and a SCE.

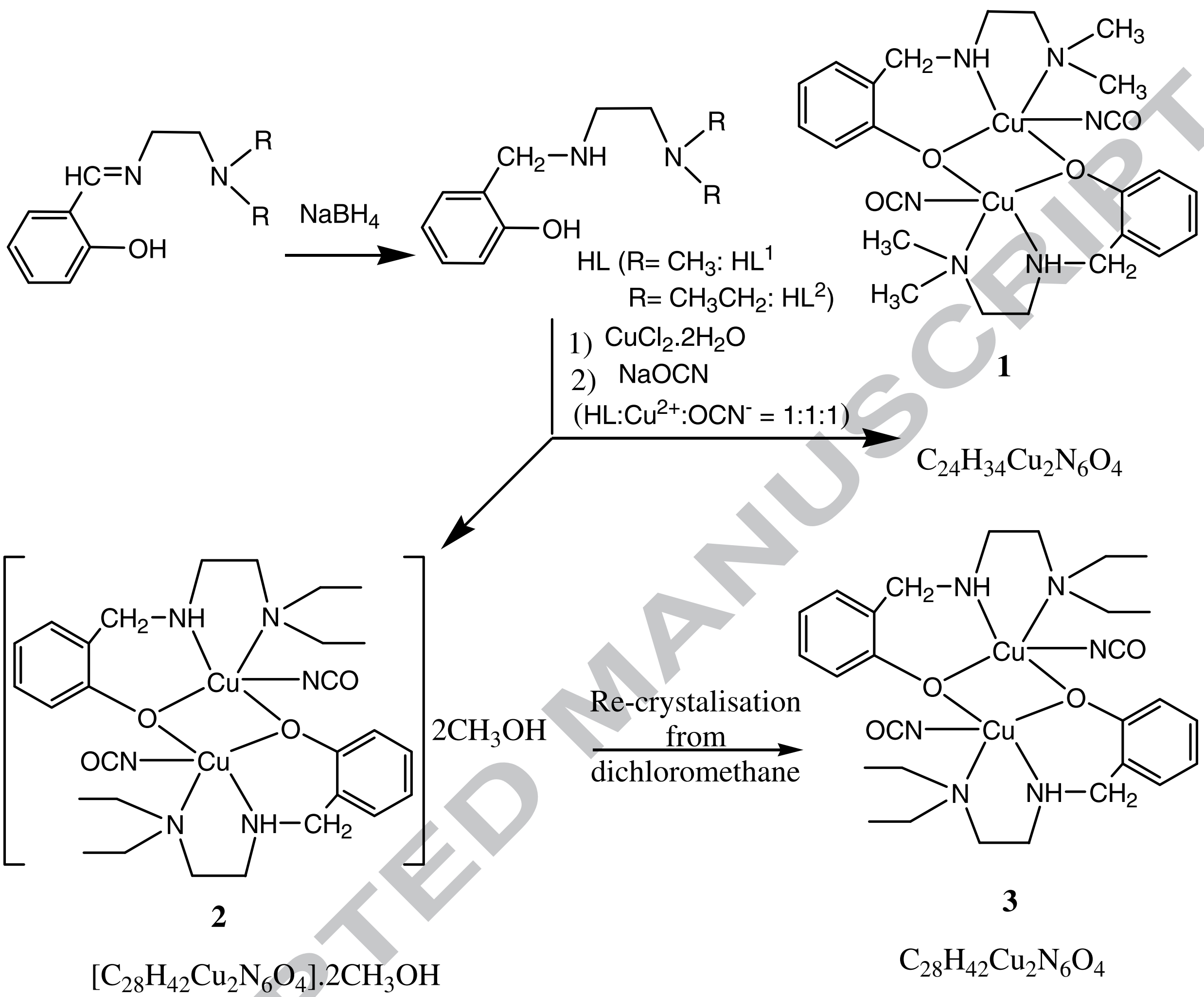
2.5. Crystal Data Collection and Refinement

Crystal data for the three crystals are given in Table 1. The independent data for **1**, **2**, and **3** respectively were collected with MoKα (λ = 0.71073 Å) radiation, using the Bruker SMART diffractometer. All structures were solved using Patterson method with the SHELXS 97 program. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. All calculations were carried out using SHELXS 97 [35], SHELXL 97 [36], PLATON 99 [37], ORTEP-32 [38] and WinGX system Ver-1.64 [39].

3. Results and Discussion

3.1. Synthesis of the Complexes

The condensation of N,N-dimethylethylenediamine and N,N-diethylethylenediamine with salicylaldehyde afforded the Schiff bases, 2-[(2-dimethylamino-ethylimino)-methyl]-phenol, 2-[(2-diethylamino-ethylimino)-methyl]-phenol, respectively. Reduction of these Schiff bases with sodium borohydride readily produced the reduced Schiff bases, HL^1, and HL^2 (Scheme 1). HL^1 on reaction with copper(II) chloride in presence of sodium cyanate in 1:1:1 molar ratios yielded compound **1**. Similarly, HL^2 on reaction with copper(II) chloride in presence of sodium cyanate in 1:1:1 molar ratios yielded compound **2**. The re-cystalisation of compound **2** from dichloromethane produced compound **3**. Compounds **2** and **3** are well crystalline products and their PXRD patterns match nicely with the simulated ones indicating that the products are not mixtures of the two compounds (Figures S1 and S2). On the other hand, thermogravimetric analysis of compound **2** shows that on heating it loses two molecule of methanol (obs. 8.74 %, calc. 8.85 %) in the temperature range 47-84 ºC (Figure S3); the PXRD patterns (Figure S4) of the desolvated product is not identical to that of **3** indicating a different crystalline form is produced upon desolvation. Compound **1** does not contain any solvent molecule and on recrystallization from acetonitrile or dichloromethane no compound other than **1** results.



Scheme 1. Formation of the complexes

3.2. IR and electronic spectra

The IR spectra of the complexes **1, 2,** and **3** exhibit a moderately strong, sharp peak at respectively 3220, 3217, and 3201 cm^{-1}, which is ascribed to the N–H stretching vibration, therefore confirming that the imine group of the Schiff base has been reduced. The complexes **1**,

2, and **3** exhibit ν-$_{CN}$ bands at 2213, 2206, and 2175 cm^{-1} respectively. The stretching vibrations are in good agreement with the literature values which show that ν_{as} appears at higher wave number as the MNC angle approaches 180° [40-44].

Electronic spectra were recorded in methanol solution, which show a single absorption band at 650, 622, and 622 nm due to the d-d transition for compounds **1, 2** and **3** respectively. At higher energy region, the ligand to metal charge transfer bands were located at 415 nm for compound **1** and 425 nm the compounds **2** and **3.**

*3.3. Description of structures of complexes **1**, **2** and **3***

The structure of $[Cu_2(L^1)_2(NCO)_2]$ (**1**) is a centrosymmetric dimer as shown in Figure 1 with each metal atom in a five-coordinate environment. Dimensions in the metal coordination sphere are given in Table 2. In the asymmetric unit, there are two independent half molecules A and B of the centrosymmetric dimers with equivalent geometries.

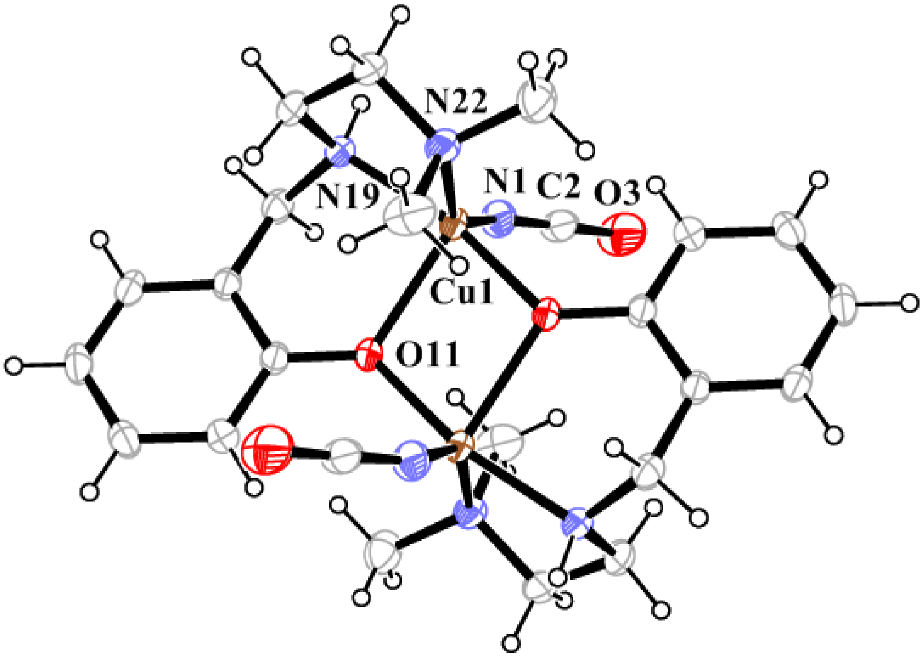
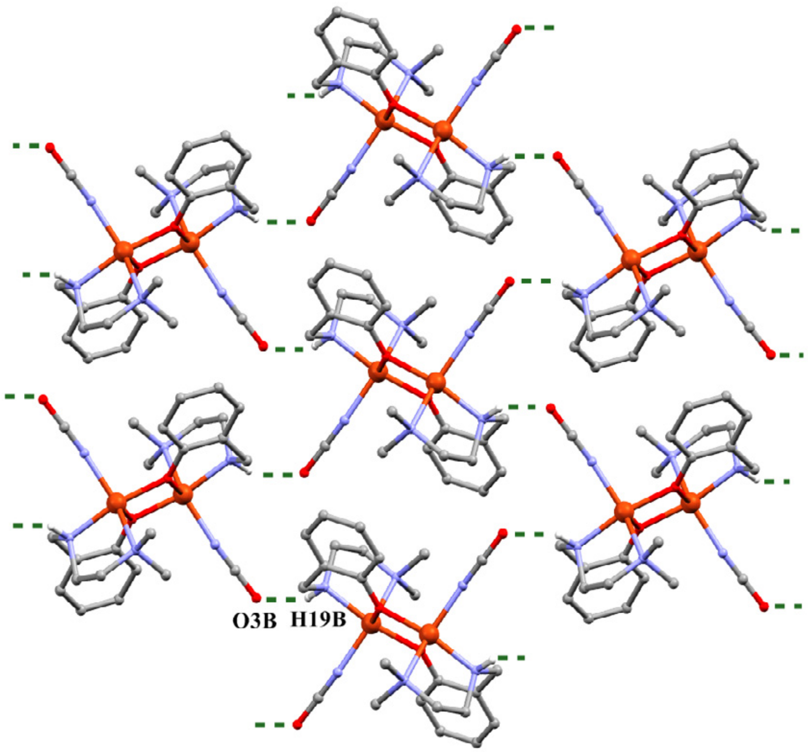


Figure 1. The centrosymmetric structure of **1** with ellipsoids at 30% probability.

The metal atom is bonded to the tridentate ligand L^1 via O(11) at 2.215(2), 2.192(2), N(19) at 2.001(2), 2.000(3) and N(22) at 2.107(3), 2.101(2) Å, together with a bridging oxygen atom O(11)^a, (^{a} = 1-x, 1-y, 2-z) from a second ligand at 1.940(2), 1.940(2) Å and a terminal OCN ligand via N(1) at 1.985(3), 1.978(3) Å for **1A** and **1B** respectively. The two Cu atoms are separated by 3.1949(5), 3.1624(5) Å and the Cu(1)–O(11)–Cu(1)^a angle are 100.30(9), 99.55(9)° for **1A** and **1B** respectively. The geometry around Cu(II) may be described as square pyramidal; the deviations of the coordinating atoms N(1), N(19), N(22), O(11)^a from the least-square mean plane through them are -0.390(3), 0.428(2), -0.409(3), 0.371(2) Å respectively for **1A** and -0.400(3), 0.441(3), -0.423(3), 0.382(2) Å respectively for **1B**. The deviation of Cu(II) from the same plane is 0.195(1), 0.221(1) Å for **1A** and **1B** respectively in the direction of chelating oxygen atom O(11) which may be considered as axially coordinated. However, the geometry around Cu(II) can also be described as trigonal bipyramid with O(11), N(1), and N(22) make up the equatorial plane which together with Cu(II) provides a r.m.s. deviations 0.0372, 0.0371 Å for **1A** and **1B** respectively. The Addison parameter (τ) [45] of the penta-coordinated Cu(II) is 0.38 (average) indicating that the geometry is a distorted square pyramid.

The hydrogen H(19B) on amine nitrogen N(19) forms a hydrogen bond to a oxygen atom O(3B) with dimensions N···O 3.024(4) Å, ∠N–H···O 154°, H···O 2.18 Å to result in a 2-D polymeric structure (Figure 2). Another polymeric 2D structure of **1** is formed by the interdimer C–H/π interactions [between H(23D) and Cg of phenyl ring with dimensions H···Cg = 2.79] and hydrogen bonding interactions between the hydrogen H(19A) and a oxygen atom O(3A) with dimensions N···O 3.192(4) Å, ∠N–H···O 131°, H···O 2.53 Å (Figure 3).



179 **Figure 2.** Hydrogen bonding polymeric structure of compound **1** (hydrogen atoms except H19B

180 omitted for clarity).

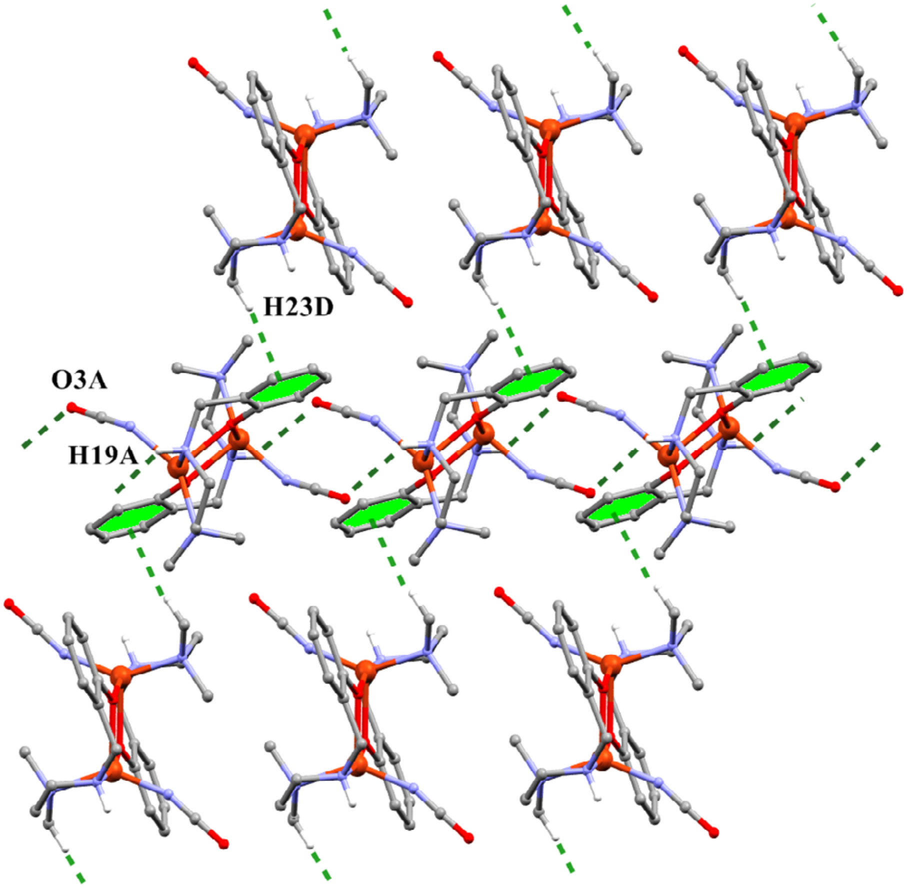
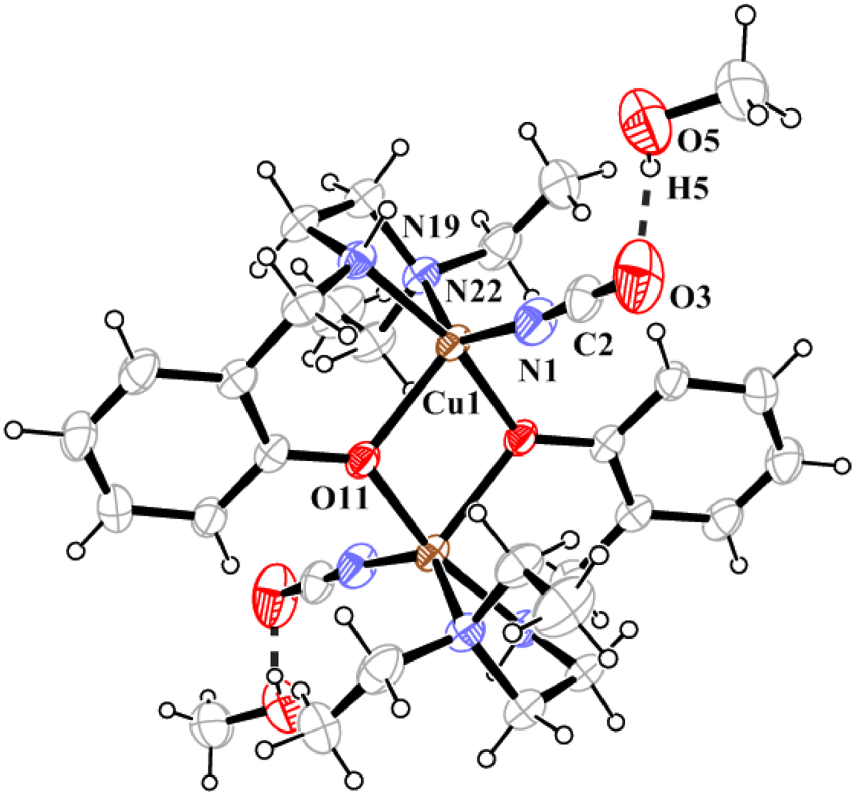


Figure 3. Polymeric 2D structure of **1** formed by the interdimer C–H/π and Hydrogen bonding interactions (hydrogen atoms except H19A and H23D omitted for clarity).

The structures of [$Cu_2(L^2)_2(NCO)_2$]·$2CH_3OH$ (**2**) and [$Cu_2(L^2)_2(NCO)_2$] (**3**) are also centrosymmetric dimers, shown in Figures 4 and 5 respectively together with the atomic numbering scheme. Dimensions in the metal coordination sphere are given in Table 2.



186 **Figure 4.** The structure of **2** with ellipsoids at 30% probability. Hydrogen bonding interactions

187 are shown in dotted lines.

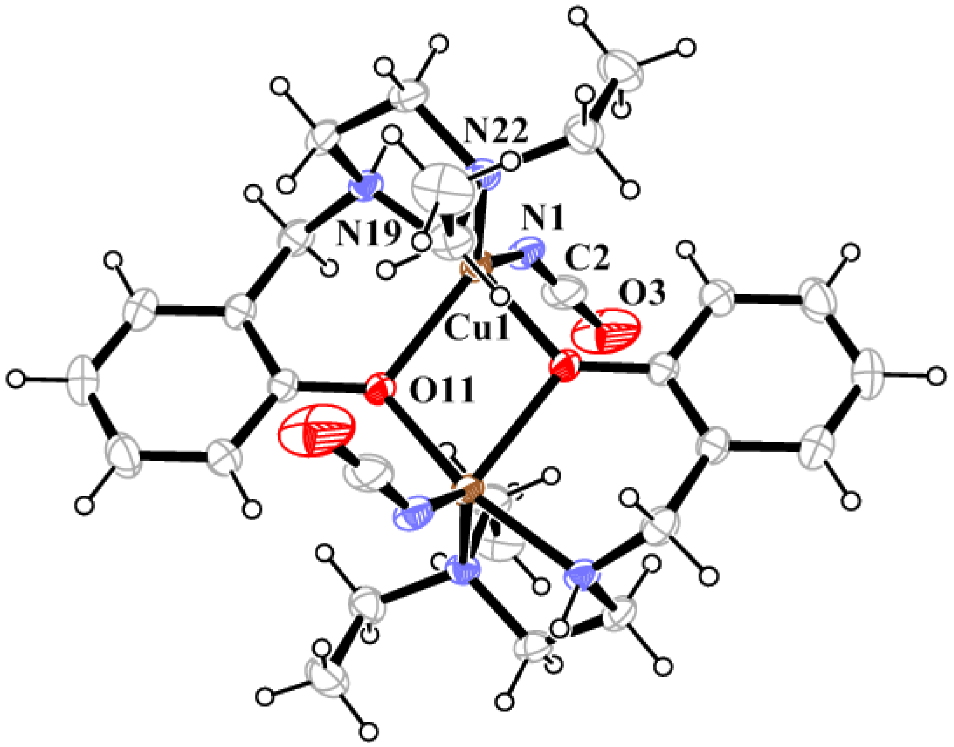


Figure 5. The centrosymmetric structure of **3** with ellipsoids at 30% probability.

In both cases the metal atoms are five-coordinate being bonded to three donor atoms of one ligand L^2 together with an oxygen atom $O(11)^a$ a = (-x, -y, -z) in **2,** and (a = (2-x,1-y,2-z) in **3**) of a second ligand L^2 and a nitrogen atom N(1) of the monodentate –NCO. Both oxygens of the two ligands L^2 bridge the two copper atoms. Bond lengths in the metal coordination sphere are Cu(1)–O(11) 2.175(4), 2.182(2) Å, Cu(1)–N(19) 1.987(4), 1.984(2) Å and Cu(1)–N(22) 2.126(4), 2.141(2) Å to the tridentate ligand L^2 with Cu(1)–$O(11)^a$ 1.939(3), 1.949(2) Å and Cu(1)–N(1) 1.994(5), 2.056(2) Å to the monodentate cyanate group for complexes **2** and **3** respectively. The deviations of the coordinating atoms N(1), N(19), N(22), $O(11)^a$ from the least-square mean plane through them are -0.449(4), 0.503(4), -0.468(4), and 0.414(3) Å respectively in **2**. -0.481(2), 0.550(2), -0.509(2), and 0.440(2) Å respectively in **3**. The deviation of Cu(II) from the same plane is 0.257(1) Å in **2** and 0.280(1) Å in **3** in the direction of chelating oxygen atom O(11) which may be considered as axially coordinated. However, the geometry around Cu(II) can also be described as trigonal bipyramid with O(11), N(1), and N(22) make up the equatorial plane which together with Cu(II) provides a r.m.s. deviations 0.0424, 0.0406 Å for **2** and **3** respectively. The Addison parameter (τ) of the penta-coordinated Cu^{II} is 0.48 in **2** and 0.53 in **3** indicating that the geometry is a distorted trigonal bipyramid with $O(11)^{a}$ and N(19) occupying axial positions. The major difference between the two complexes is the Cu(1)-N(1)-C(2) angles of cyanate group, which is small (139.5°) in **2** compare to that in **3** (172.3°) indicating that the orientation of the OCN^{-} ligand in both the complexes are not alike.

Compounds **2** and **3** are the solvomorphs as **2** has an additional methanol molecule which is uncoordinated but is H-bonded into the lattice, linking the complex molecules together**.** A helical like hydrogen bonding interactions of H(19) with O5 and H(5) with O3 (Figure 6a) lead to the formation of a 2-D supramolecular structure (Figure 7) with dimensions N(19)···O(5) 2.900(7) Å, H(19)···O(5) 2.03 Å, ∠N(19)–H(19)–O(5) 160° and O(5)···O(3) 2.755(8) Å, H(5)···O(3) 1.94 Å, ∠O(5)–H(5)–O(3) 170° respectively (Table 3). There are also hydrogen bonding interactions of H(13) with N(1) and H(21A) with O(3) with dimensions C(13)···N(1) 3.258(8) Å, H(13)···N(1) 2.59 Å, ∠C(13)–H(13)–N(1) 129°, and C(21)···O(3) 3.413(8) Å, H(21A)···O(3) 2.60 Å, ∠C(21)–H(21A)–O(3) 142° (Figure 6b)**.** In complex **3,** a 2-D supramolecular structure (Figure 8) is formed through hydrogen bonding with dimensions

N(19)···N(1) 3.213(3) Å, H(19)···N(1) 2.34 Å, ∠N(19)–H(19)–N(1) 162°, and C(21)···O(3) 3.363(5) Å, H(21B)···O(3) 2.51 Å, ∠C(21)–H(21B)–O(3) 147° (Table 3).

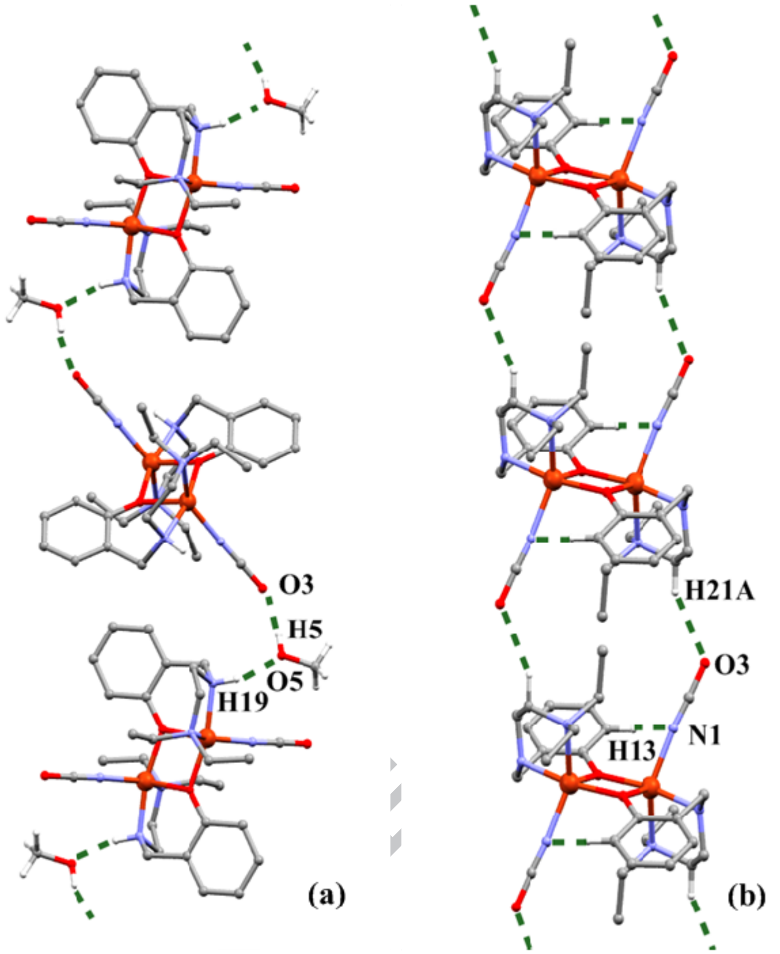
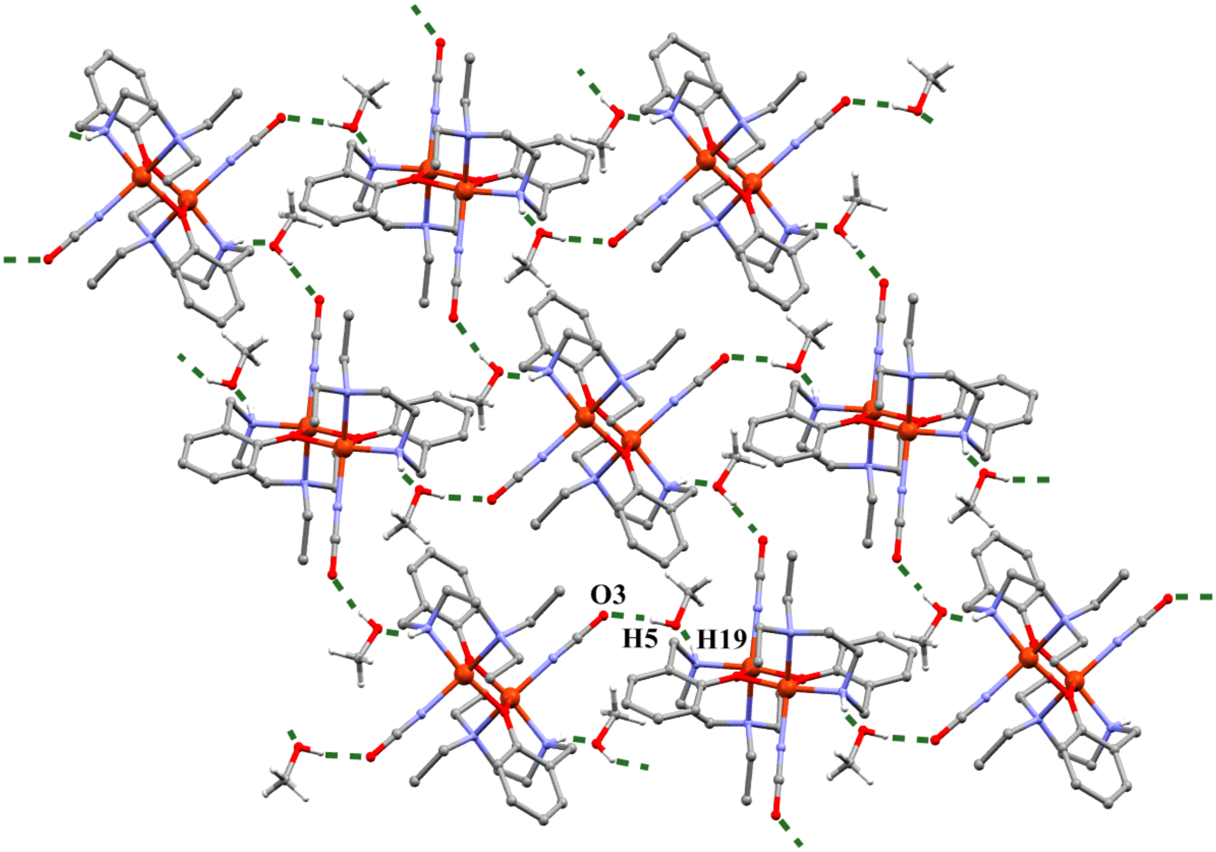


Figure 6. (a) Helical like hydrogen bonding interactions (all hydrogen atoms of the dimeric molecule except H19 are omitted for clarity). (b) Intra and intermolecular hydrogen bonding interactions of compound **2** (hydrogen atoms except H13 and H21A omitted for clarity).



223 **Figure 7.** Hydrogen bonding polymeric structure of compound **2** (all hydrogen atoms of the
224 dimeric molecule except H19 are omitted for clarity).

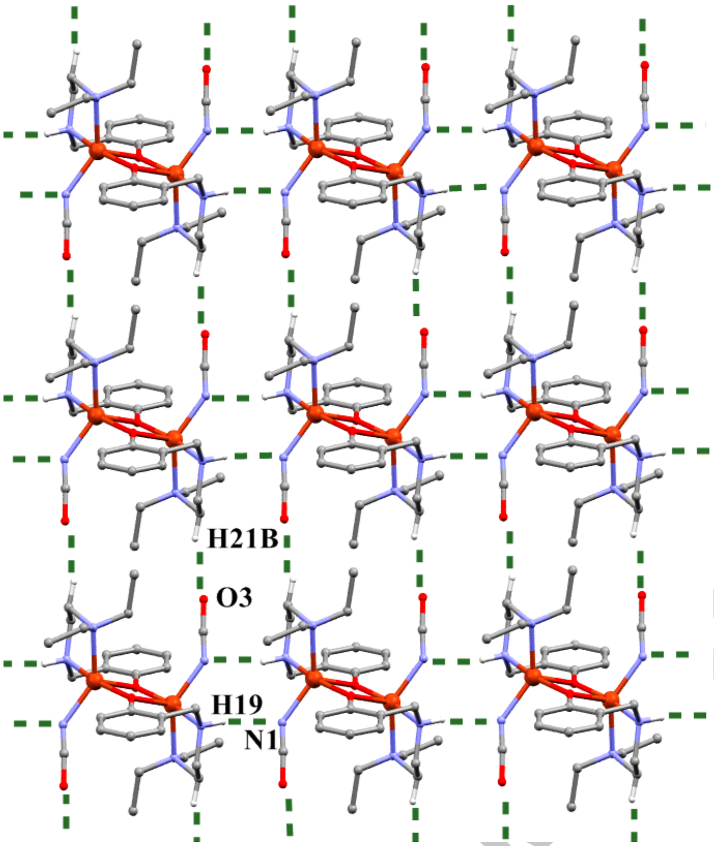


Figure 8. Hydrogen bonding 2D structure of compound **3** (hydrogen atoms except H19 and H21B omitted for clarity).

3.4. Kinetic Studies for Catecholase Activity

In most studies of the catecholase activity of model complexes, 3,5-di-*tert*-butylcatechol (3,5-DTBC) has been chosen as the substrate. The oxidation product 3,5-di-*tert*-butylquinone (3,5-DTBQ) is very much stable and exhibits a maximum absorption at 390 nm in pure methanol. Prior to a detailed kinetic study, it is necessary to check the ability of the dinuclear complexes to oxidize 3,5-DTBC. For this purpose, 10^{-4} (M) solutions of complexes **1** and **2** were treated with 100 equivalents of 3,5-DTBC under aerobic condition in methanol solution.

Immediately after addition of substrate 3,5-DTBC to the solutions of the catalysts, the absorption peak at 390 nm (ε = 1900 M^{-1} cm^{-1}), which is indicative of an oxidation from 3,5-DTBC corresponding to quinone (3,5-DTBQ), increased in size thus showing considerable catecholase activity, as shown in Figure 9 (for complex **2**), and S5 (for complex **1**), when compared to the inactive $Cu(ClO_4)_2{\cdot}6H_2O$. (Figure S6).

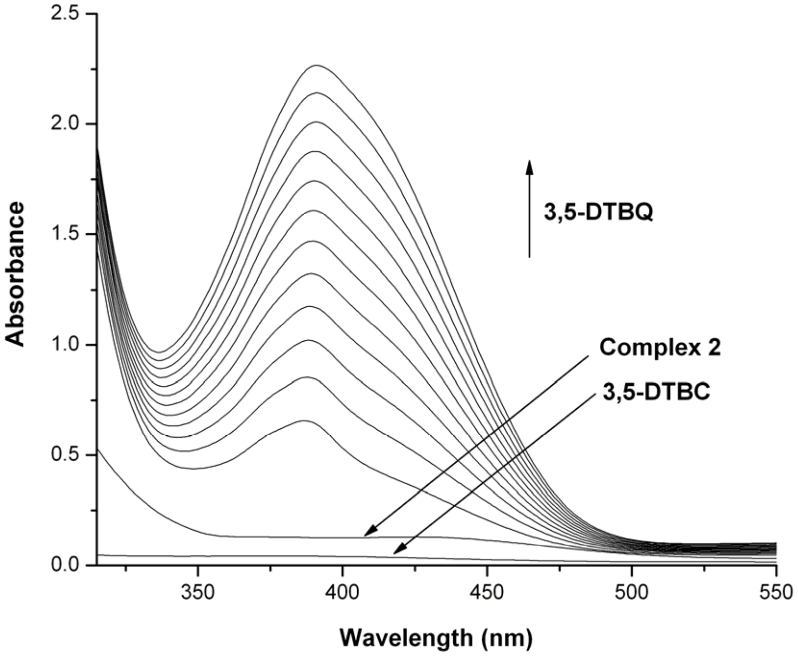


Figure 9. Increase in absorbance after addition of 100 equivalents of 3,5-DTBC to a methanolic solution containing complex **2** (10^{-4} M). The spectra were recorded every 10 min.

The kinetic study of the oxidation of 3,5-DTBC to 3,5-DTBQ by the complexes was carried out by monitoring the increase in absorbance at 390 nm by the initial rates method. The rate constant for a particular complex-substrate mixture was determined from the $\log[A_\alpha/(A_\alpha - A_t)]$ vs. time plot. To determine the dependence of the rates on the substrate concentration and various kinetic parameters, solutions of the complexes **1**, and **2** were studied using increasing concentrations of 3,5-DTBC (from 10 to 100 equivalents) under aerobic conditions at a complex concentration of 10^{-4} (M). A first-order dependence was observed at low concentrations of the substrate, whereas a saturation kinetics was found at higher concentrations of the substrate for all the complexes shown in Figure 10 (for complex **2**), and Figure S7 (for complex **1**). This dependence on the substrate concentration indicates a catalyst-substrate binding to be an initial step in the catalytic mechanism. A treatment on the basis of the Michaelis-Menten approach, originally developed for enzyme kinetics, was therefore applied and linearized by means of a Lineweaver-Burk plot to calculate the Michaelis-Menten constant (K_M) and the maximum initial rate (V_{max}) [46]. The k_{cat} values can be calculated by dividing the V_{max} values by the concentration of the corresponding complexes.

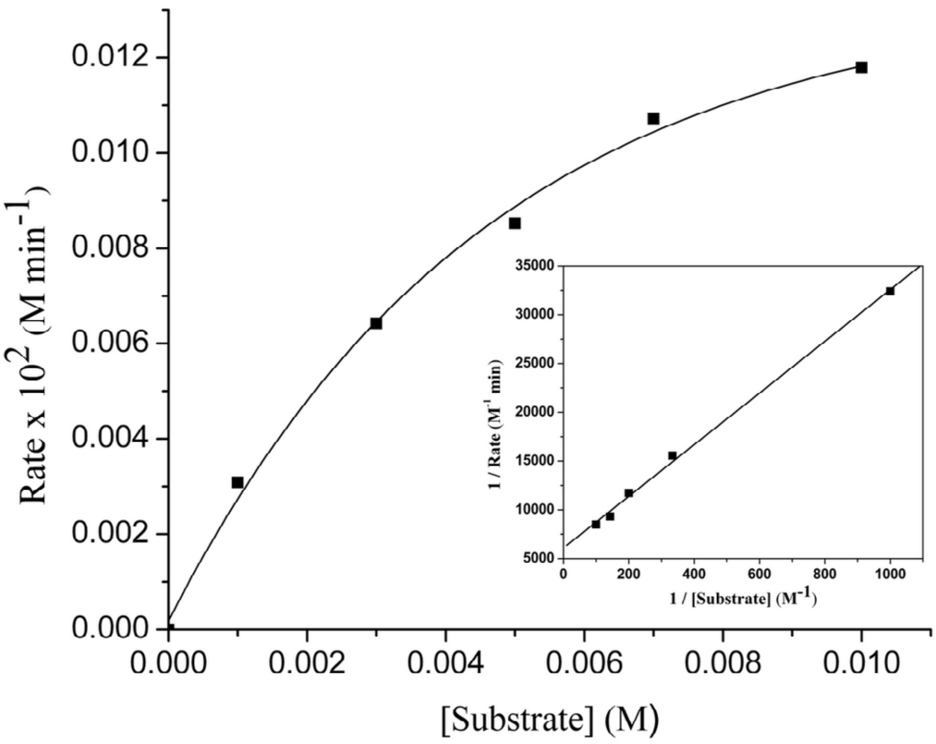


Figure 10. Plot of initial rates vs. substrate concentrations for aerobic oxidation of 3,5-DTBC by complex **2**. The inset shows the Lineweaver-Burk plot.

The data obtained from the Lineweaver-Burk plot model are used for a comparison of catalytic activity towards the oxidation of 3,5-DTBC as shown in Table 4. The catecholase activity of compound **2** (k_{cat} = 98.4 h^{-1}) is slightly higher than that of compound **1** (k_{cat} = 64.2 h^{-1})**.** The cyclic voltammograms of complexes **1** and **2** show irreversible cathodic peaks E(red)$_1$ at – 0.65, -0.60 V and E(red)$_2$ at -1.11 and -1.02 V respectively (Figure S8). This reduction peaks tentatively assigned to the one electron process $Cu^{II}Cu^{II} \rightarrow Cu^{II}Cu^{I}$ and $Cu^{II}Cu^{I} \rightarrow Cu^{I}Cu^{I}$. Many research groups have attempted to correlate the redox properties of the copper(II) complexes with their catecholase activity [5,47-50]. Casella and co-workers [51] succeeded in calculating the reaction rates for the two successive steps of the catalytic reaction (a fast stoichiometric reaction between a dicopper(II) complex and a catechol and a slower catalytic reaction), and showed a clear dependence of the reaction rate in the first stoichiometric step on the Cu^{II}/Cu^{I} reduction potential. As this step involves the electron transfer from the bound catecholate to the dicopper(II) center, this observation is easily understood. The lower Cu^{II}/Cu^{I} reduction potential of complex **2** than that of complex **1** favours the oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) to 3,5-di-*tert*-butylquinone (3,5-DTBQ) but the overall reaction rates obviously depend on many factors, i.e. the rate of the reoxidation of the dicopper(I) species by dioxygen, the rate of the catechol oxidation by the formed peroxo-dicopper intermediate etc.

4. Conclusions

The tridentate reduced Schiff base ligands 2-[(2-dimethylamino-ethylamino)-methyl]-phenol (HL^1) and 2-[(2-diethylamino-ethylamino)-methyl]-phenol (HL^2) with Cu(II) and cyanate anions have affoarded two related phenoxido bridged dinuclear Cu(II) complexes. The coordination environment of the Cu(II) ions in both the complexes are square pyramidal but with different degrees of distortion toward a trigoanal bipyramid. Re-crystalisation of compound **2** from dichloromethane produced another related desolvated phenoxido bridged dinuclear Cu(II) complex **3** having the environment around the copper ions is an intermediate between the trigonal bipyramid and a square based pyramid. The compounds **2** and **3** are solvomorphs. The strong and weak hydrogen bonds between solvent and solute molecules facilitates or retention of organic solvents in crystals of **2**. The slightly higher catecholase activity of compound **2** than **1** can be explained with the help of their respective reduction potensial.

Acknowledgements

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Appendix A. Supplementary material

CCDC 926840, 926841 & 926842 contain the supplementary crystallographic data for **1, 2** and **3**, respectively. These data can be obtained free of charge via 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; or e-mail: deposit @ccdc.cam.ac.uk.

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Table 1. Crystal data and structure refinement of complexes **1, 2** and **3**

	1	**2**	**3**
Formula	$C_{24}H_{34}Cu_2N_6O_4$	$C_{30}H_{50}Cu_2N_6O_6$	$C_{28}H_{42}Cu_2N_6O_4$
M	597.67	717.86	653.78
Crystal System	Monoclinic	Orthorhombic	Monoclinic
Space Group	$P2_1/c$	*P*bca	$P2_1/n$
a/Å	18.0501(7)	9.455(5)	9.953(4)
b/Å	17.5908(6)	17.355(5)	8.677(3)
c/Å	8.3961(3)	20.472(5)	17.664(7)
α/°	90	90	90
β/°	103.189(1)	90	102.830(4)
γ/°	90	90	90
V/Å^3	2595.57(16)	3359(2)	1487.4(10)
Z	4	4	2
D_c/g cm^{-3}	1.530	1.419	1.460
μ/mm^{-1}	1.681	1.316	1.473
F (000)	1240	1512	684
R(int)	0.058	0.103	0.032
Total Reflections	31393	23476	10302
Unique reflections	5453	3388	2823
$I>2\sigma(I)$	3855	2006	2388
R1, *w*R2	0.0390, 0.0969	0.0654, 0.1885	0.0304, 0.0802
Temp (K)	296	293	296

Table 2. Bond distances (Å) and angles (°) for complexes **1, 2** and **3**

	Complex **1A**	Complex **1B**	Complex **2**	Complex **3**
Cu(1)–O(11)	2.2152(18)	2.192(2)	2.175(4)	2.182(2)
Cu(1)–N(19)	2.001(2)	2.000(3)	1.987(4)	1.984(2)
Cu(1)–O(11)[a]	1.940(2)	1.944(2)	1.939(3)	1.949(2)
Cu(1)–N(22)	2.107(3)	2.101(2)	2.126(4)	2.141(2)
Cu(1)–N(1)	1.985(3)	1.978(3)	1.994(5)	2.056(2)
O(11)–Cu(1)–N(19)	89.05(9)	88.60(10)	88.83(14)	88.93(7)
O(11)–Cu(1)–O(11)[a]	79.70(8)	80.45(9)	79.50(13)	78.56(6)
N(19)–Cu(1)–O(11)[a]	166.60(9)	167.06(10)	166.70(16)	166.33(7)
O(11)–Cu(1)–N(22)	112.56(9)	109.29(9)	137.62(16)	112.45(7)
N(19)–Cu(1)–N(22)	84.17(10)	84.38(10)	83.53(15)	84.04(8)
N(22)–Cu(1)–O(11)[a]	93.38(9)	92.70(10)	94.72(15)	95.60(7)
N(1)–Cu(1)–O(11)	101.97(9)	107.55(11)	110.28(16)	112.16(8)
N(1)–Cu(1)–N(19)	90.37(11)	90.29(11)	89.99(18)	89.41(8)
N(1)–Cu(1)–O(11)[a]	99.01(10)	99.53(11)	99.99(18)	100.33(8)
N(1)–Cu(1)–N(22)	144.88(10)	142.59(11)	137.62(16)	134.72(8)

Symmetry element [a] = (1-x,1-y,2-z) in **1A**, (-x,1-y,1-z) in **1B**, (-x, -y, -z) in **2,** (2-x,1-y,2-z) in **3**.

Table 3. Hydrogen bonding distances (Å) and angles (°) for the complexes **1, 2,** and **3**

Complex	D–H···A	D–H (Å)	A···H (Å)	D···A (Å)	∠D–H–A (°)
1A	N(19A)–H(19A)···O(3A)[b]	0.91	2.53	3.192(4)	131
1B	N(19B)–H(19B)···O(3B)[c]	0.91	2.18	3.024(4)	154
2	N(19)–H(19)···O(5)[d]	0.91	2.03	2.900(7)	160
	O(5)–H(5)···O(3)[e]	0.82	1.94	2.755(8)	170
	C(13)–H(13)···N(1)[a]	0.93	2.59	3.258(8)	129
	C(21)–H(21A)···O(3)[e]	0.97	2.60	3.413(8)	142
3	N(19)–H(19)···N(1)[f]	0.91	2.34	3.213(3)	162
	C(21)–H(21B)···O(3)[g]	0.97	2.51	3.363(5)	147

Symmetry element [b] = (1-x,1-y,3-z), [c] = (x,1/2-y,1/2+z), [d] = (-1/2+x,1/2-y,z), [e] = (1+x,y,z), [f] = (2-x,-y,2-z), [g] = (-1+x,y,z)

Table 4. Kinetic parameters for the oxidation of 3,5-DTBC to 3,5-DTBQ mediated by complexes **1, 2** and some other related compounds.

complex	V_{max} (M min^{-1})	K_M (M)	k_{cat} (h^{-1})	Ref
1	$(1.07\pm0.02)\times10^{-4}$	$(2.35\pm0.03)\times10^{-3}$	64	present work
2	$(1.64\pm0.01)\times10^{-4}$	$(4.34\pm0.12)\times10^{-3}$	98	present work
$[Cu_2(L^1)(OH)(EtOH)(H_2O)][ClO_4]_2.H_2O$	1.69×10^{-4}	2.4×10^{-4}	214	11
$[Cu_2(L^5)(OMe)][ClO_4]_2.2MeOH$	5.22×10^{-4}	2.3×10^{-3}	33	11
$[Cu_2(L^6)(OMe)(MeOH)\text{-}(ClO_4)]ClO_4$	7.56×10^{-5}	3.1×10^{-4}	48	11
$[Cu_2(L^7)(OMe)(MeOH)(ClO_4)]ClO_4$	6.78×10^{-5}	1.4×10^{-3}	43	11
$[Cu_2(H_2L)(\mu\text{-}OH)](ClO4)_2$	8.0×10^{-5}	11.6×10^{-4}	28	47
$[Cu_2(L)(H_2O)_2]PF_6$	10.15×10^{-5}	12.2×10^{-4}	36	47

Graphical abstract (synopsis)

Solvomorphism and catecholase activities of bis(μ-phenoxido)dicopper(II) complexes

Apurba Biswas, Lakshmi Kanta Das, Ashutosh Ghosh

Three phenoxido bridged dinuclear Cu(II) complexes, $[Cu_2(L^1)_2(NCO)_2]$ (**1**), $[Cu_2(L^2)_2(NCO)_2]\cdot 2CH_3OH$ (**2**) and $[Cu_2(L^2)_2(NCO)_2]$ (**3**) obtained from the reduced Schiff base ligands show that the Cu(II) ions are penta-coordinated having the geometry intermediate between distorted square pyramid and trigonal bipyramid. The compounds **2** and **3** are pseudopolymorphs. The complexes show moderate catecholase activity.

Graphical abstract (picture)

Solvomorphism and catecholase activities of bis(μ-phenoxido)dicopper(II) complexes

Apurba Biswas, Lakshmi Kanta Das, Ashutosh Ghosh