

Electronic Supplementary Information

Aerobic Oxidation of 1,10-Phenanthroline to Phen-dione Catalyzed by Copper(II) Complexes of a Benzimidazolyl Schiff Base

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Experimental Section, Physical measurements and Structure Refinement

Synthesis of Ligand with reaction scheme S1 and its ORTEP diagram with UV-Visible Spectra (Fig. S1 & S2)

Synthesis of copper(II) complexes and its UV-Visible spectra (Fig. S3)

Oxidation of 1,10-Phenanthroline with reaction scheme S2

Role of molecular oxygen

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Drop in the d-d band intensity of complex (1) under ODC (Fig. S5)

¹H and ¹³C-NMR Spectra of Ligand (Fig. S6, S7)

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Cu-Phenanthroline complex band (Fig. S9)

Crystallographic Data and Selected Bond length and angle Table

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Experimental

Materials

All the reagents used were of analytical grade. β -alanine, *N*-methyl-*o*-phenylenediamine, 2-hydroxy naphthaldehyde were purchased from Sigma-Aldrich and all other chemicals and solvents were of analytical grade and used as received. *N*-methyl-2-Aminoethylbenzimidazolyl dihydrochloride was prepared following the procedure reported by Cescon and Day¹.

Physical Measurements

Elemental analyses of Copper(II) complexes were obtained with a Gmbh VarioEL V3.00 Elemental analyzer from USIC, University of Delhi, Delhi India. Electronic spectra were recorded on an Shimadzu 1601 spectrometer at the Department of Chemistry, University of Delhi. IR spectra were recorded in the solid state as KBr pellets on a Perkin-Elmer FTIR-2000 Spectrometer in the region of 400-4000 cm^{-1} . The single crystal diffraction data were collected on an X'Calibur single crystal X-ray diffractor having CCD camera at USIC, University of Delhi, Delhi, India. The EPR measurements were made on a X-band Bruker system ESP300, equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter from Indian Institute of Technology, Bombay (India).

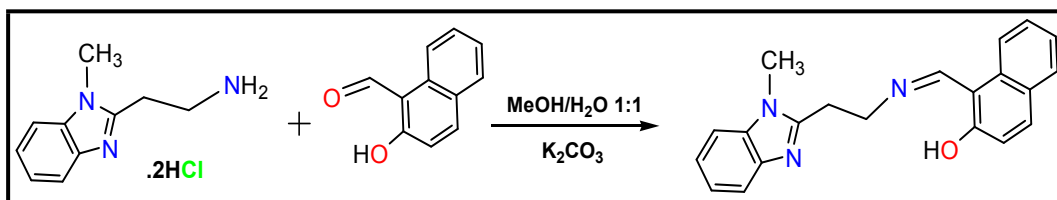
X-ray data Collection, Structure Determination and Refinement

Single crystals of Schiff base ligand **HL**, and its complexes suitable for X-ray diffraction studies were grown by slow evaporation in methanol. The intensity data of ligand **HL** was collected at 298(2) K and its complex **(1)** was collected at 150(2) K and complex **(2)** at 298(2) K on an X'calibur CCD diffractometer with graphite monochromatized Mo/ $K\alpha$. Radiation ($\lambda=0.71073 \text{ \AA}$) from USIC. For **HL**, a total of 13105 reflections were measured of which 3372 were unique and 2198 were considered observed ($I > 2\sigma(I)$). For complex **(1)**, a total of 14366 reflections were measured of which 3516 were unique and 3236 were considered observed ($I > 2\sigma(I)$). For Complex **(2)**, a total of 15920 reflections were measured of which 3544 were unique and 2506 were considered observed ($I > 2\sigma(I)$). The data were corrected for Lorentz and polarization effects. Multi-scan absorption correction was applied. The structure was solved by direct methods using SHELXS-97² and refined by full-matrix least-squares refinement techniques on

F^2 , using SHELXL-97². All calculations were done with the help of WINGX programme³ For the molecular graphics, the programme Diamond2⁴ and Mercury⁵ were used. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically with U_{iso} values of 1.2 times the U_{iso} values of their respective carrier atoms. The final residual index for **HL** are; R 0.0455, R_w 0.1067 for the observed and R 0.0591, R_w 0.1134 for all reflections using 231 parameters and zero restraint. The final residual index for complex (1) is; R 0.0335, R_w 0.0859 for the observed and R 0.0372, R_w 0.0859 for all reflections using 262 parameters and zero restraints. The final residual index for **(2)** are; R 0.0617, R_w 0.1245 for the observed and R 0.0772, R_w 0.1302 for all reflections using 245 parameters and zero restraint. Details of the crystallographic data and structure refinement for ligand **HL**, and its complexes are given in Table S1 and bond lengths are given in table S2.

Synthesis of Schiff base Ligand (HL).

N-Methyl-2-aminoethyl benzimidazole (AB.2HCl) was dissolved in water and neutralized by adding aqueous K_2CO_3 . A stirred methanolic solution of 2-hydroxy-1-naphthaldehyde was added slowly to the above solution, after some time yellow solid were separated (Scheme S1). The solid was filtered off, washed with water, and petroleum ether, dried in vacuo over P_2O_5 . It was finally recrystallized from acetonitrile and analyzed for the composition $C_{21}H_{19}N_3O$. Yield: 82%. m.p.: 224°C. Anal. Found (Calc.) for $C_{21}H_{19}N_3O$: C 76.3 (76.5), H 5.6 (5.7), N 12.7 (12.7); IR (KBr, cm^{-1}): $\nu_{(C=N-C=C)}$ 1362, $\nu_{(NH)(H-bonded)}$ 2919, $\nu_{(C=N)}$ 1635; $\nu_{C=C}$ benzene 741. 1H -NMR(d_6 -DMSO, δ ppm): 13.9(s, 1H, OH), 12.2(s, 1H, NH), 9.1(s, 1H, -CH=N-), 7.9(d, 1H, aromatic), 6.6-7.6(d, m, 7H, aromatic), 4.1(t, -CH₂-), 3.3(t, -CH₂-), 3.7(s, -CH₃-) (1H -NMR Fig. S6, ^{13}C -NMR Fig. S7). UV-Vis λ_{max}/nm ($\log \epsilon$) in DMF: 271(3.9), 283(3.7), 306(3.8), 402(3.7), 422(3.7) (Fig. S1)



Scheme S1. Reaction Scheme for the preparation of ligand *N*-Methyl benzo-imidazol-2-yl ethylimino methyl naphthal-2-ol.

SCXRD Data of the ligand reveals that one hydrogen is deprotonated from the hydroxyl group of naphthaldehyd-2-ol and binds to the N atom of the imine group (Figure S1). The hydrogen on azomethine nitrogen is involved in intramolecular H-bonding with naphthalene oxygen, N3-H...O1 (1.859 Å, $i = -x, +y, -z+1/2$) and benzimidazole nitrogen, N3-H...N2 (2.507 Å, $i = -x, +y, -z+1/2$). Bond angles and bond distances between the atoms are shown in Table S2. UV spectra of the ligand is shown in fig. S2.

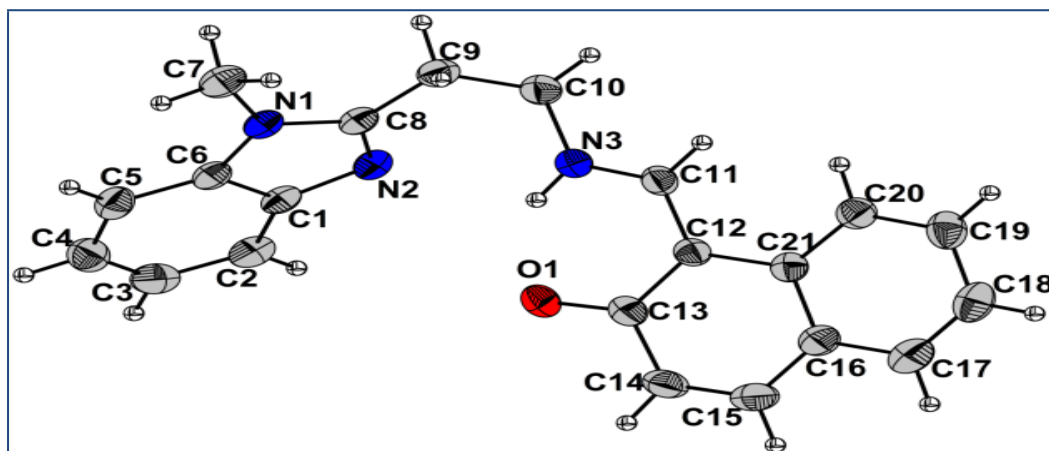


Figure S1. ORTEP diagram of the ligand (HL) drawn in 30% thermal probability ellipsoid showing atomic numbering. The ligand crystallizes in the monoclinic lattice, space group $P2_1/c$ with cell parameters, $a = 13.1445(8)$ Å, $b = 8.7158(5)$ Å, $c = 15.1599(11)$ Å, $\alpha = 90^\circ$, $\beta = 99.094(11)^\circ$, $\gamma = 90^\circ$ and $Z = 4$.

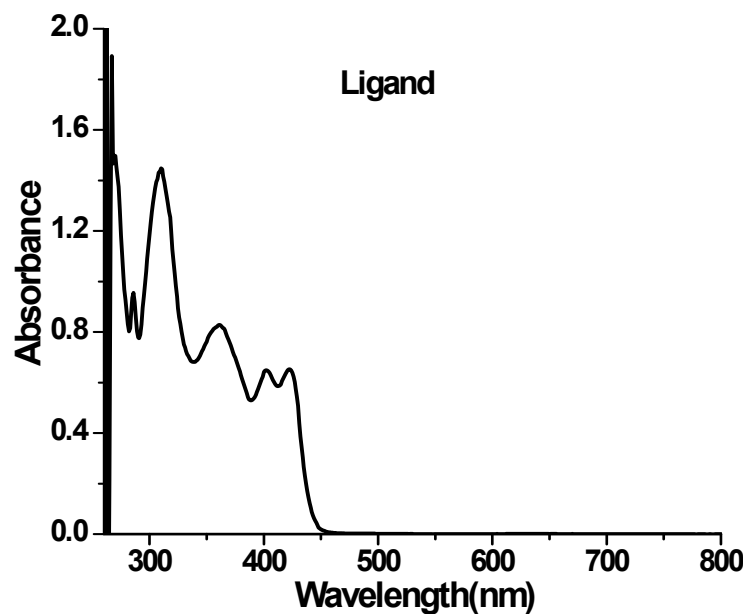


Figure S2. UV-Visible Spectra of Ligand *N*-Methyl benzo-imidazol-2-yl ethylimino methyl naphthal-2-ol [$C_{21}H_{19}N_3O$] shows four band in UV region.

Preparation of [Cu(L)NO₃] (1)

Cu(NO₃)₂ · 3H₂O (72 mg, 0.30 mmol) dissolved in 5 ml MeOH was added dropwise with stirring to a solution of Ligand (100 mg, 0.30 mmol) in 15 ml MeOH and the resulting reaction mixture was warmed up to ~80°C for 2h. Thereafter the reaction mixture was concentrated to one half of its volume on a water bath and allowed to stand at room temperature. Green colored solid was formed, washed with cold methanol, filtered, air dried. The compound analyzed for the composition C₂₁H₁₈CuN₄O₄. Yield: 74%. m.p.: 262°C. Anal. Found(Calc.): C 55.4(55.5), H 4.1(4.1), N 12.5(12.3); Selected IR(KBr, cm⁻¹); ν_(-C=N-C=C-) 1458, ν_{(NH)(H-bonded)} 3067, ν_(C=N) 1625, ν_{C=C} benzene 747; UV-Vis λ_{max}/nm(log ε) in DMF: 272(4.1), 302(3.9), 314(3.9), 386(3.6), 628(2.1) (Fig. S3)

Preparation of [Cu(L)Cl] (2)

This complex was prepared by following a procedure as reported above except that CuCl₂·2H₂O (51 mg, 0.30 mmol) was used for complexation. Green colored crystals were obtained by allowing the reaction mixture to stand for a few days at room temperature. The compound was filtered, air dried and it analyzed for the composition C₂₁H₁₈ClCuN₃O. Yield: 75%; m.p.: 215°C. Anal. Found(Calc.): C 59.2(59.0), H 4.5(4.2), N 9.8(9.8) Selected IR(KBr, cm⁻¹); ν_(-C=N-C=C-) 1459, ν_{(NH)(H-bonded)} 3052, ν_(C=N) 1618, ν_{C=C} benzene 750; UV-Vis λ_{max}/nm(log ε) in DMF: 273(4.4), 279(4.2), 317(4.1), 392(3.9), 646(2.2) (Fig. S3).

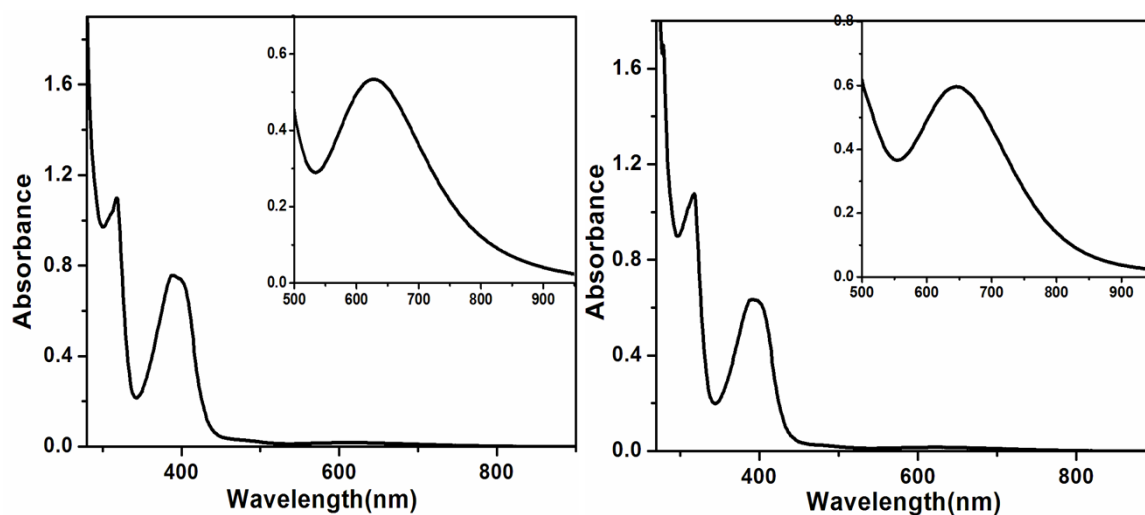


Figure S3. UV-Visible Spectra of complexes [Cu(L)NO₃] (1) (Left) and [Cu(L)Cl] (2) (Right). Inset shows d-d transition in visible region.

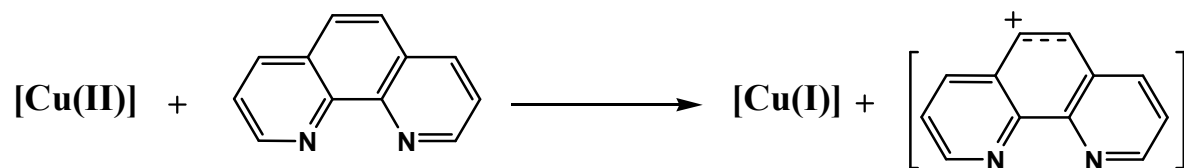
Oxidation of 1,10-Phenanthroline

The complexes [Cu(L)NO₃] (**1**) and [Cu(L)Cl] (**2**) catalyze the oxidation of 1,10-phenanthroline at room temperature in the presence of molecular O₂ in methanol. A solution of complex (2.5 mg, 0.0056 mmol in 3 ml MeOH, final concentration 1.86 mM) under saturating O₂ condition displays a broad band in the visible region at $\lambda_{\text{max}} = 628$ nm. 0.056 mmol of substrate (1,10-phenanthroline) was added to above methanolic solution (final concentration 18.6 mM). The ratio of catalyst: substrate is 1:10. The reaction was monitored by UV-vis spectroscopy. A new band starts to increase in intensity at $\lambda_{\text{max}} = 480$ nm (Fig. 3, S4). The absorbance of the reaction mixture was monitored at 480 nm. Scanning was continued after every 25 min. The band increases in intensity with the passage of time confirming the formation of 1,10-phenanthroline-5,6-dione.

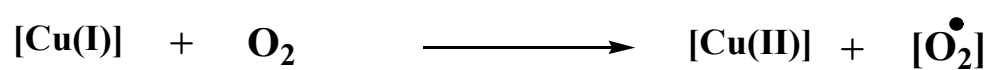
The oxidation reaction between 1,10-phenanthroline and dioxygen in presence of catalytic amount of complex was carried in 3ml of methanolic solution at room temperature. The amount of 1,10-phenanthroline was varied as 0.056, 0.039, 0.028, 0.016 and 0.0056 mmoles. The final concentrations were 18.6 mM, 13.0 mM, 9.33 mM, 5.33 mM and 1.86 mM in 3.0 ml solution respectively. The amount of catalyst 0.0056 mmoles, final concentration 1.86 mM was fixed. The ratio of catalyst to substrate are 1:10, 1:7, 1:5, 1:3 and 1:1 {Fig. 4(a)(A-E)} respectively. The same set of experiment was followed by changing the catalyst using [Cu(L)Cl] (**2**) and are compared. The relative velocity for the formation of phen-dione was calculated by considering initial slope of the absorbance ($\lambda_{\text{max}} = 480$ nm) vs time plot, fig. 4A & B, and is found to be lower for Cu(L)Cl (**2**) as compared to the Cu(L)NO₃ (**1**) by 8.4 %. To isolate the phen-dione and obtain a turnover for the catalyst, a reaction was carried out under similar condition except that the concentration of substrate to catalyst ration was to 25:1. The final product was isolated by preparative thin layer chromatography (10% Ethyl acetate: Pet. Ether solution). The R_f of isolated product is 0.78 while that of the unreacted Substrate is 0.43. The identity of isolated product is confirmed by ¹H-NMR (Fig. S8, ESI). Turnover number =16.0.

Tentative mechanism for the oxidation of 1,10-phenanthroline

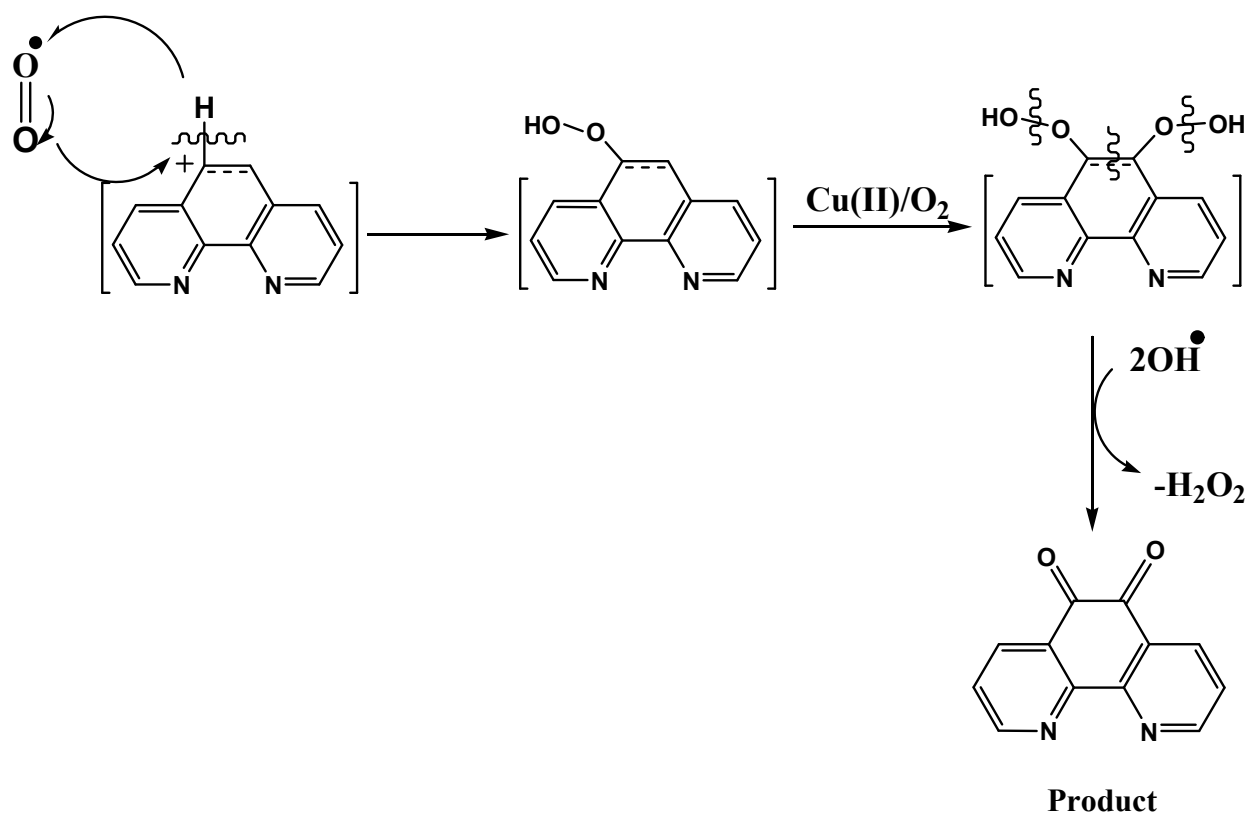
Step I



Step II



Step III



Scheme S2. Reaction scheme for catalysis

The area of the EPR single of parent complex and successive time dependent changes was obtained. It is found that the parent complex area of the EPR spectrum of the is 11673 unit and drop to a value of 8056 unit, 5281 unit and 1297 unit respectively as the catalysis proceed (Fig. 6).

Role of Molecular Oxygen

In order to determine the role of O₂, the oxidation reaction was carried out using Cu(L)NO₃ (**1**) as described earlier, however oxygen present in solvent (HPLC MeOH) was first removed by a freeze–thaw cycle. This was repeated at least 2–3 times to remove the dissolved oxygen. Subsequently the catalyst and substrate were mixed in the same ratio [1:10 in mmoles] in this oxygen depleted MeOH under nitrogen atmosphere in a septum sealed two neck flask. This mixture was then immediately syringed into a nitrogen flushed septum sealed UV-quartz cell and the reaction was monitored spectrophotometrically {Fig. 3(B)}. The Loss in the d-d band intensity of complex (**1**) under oxygen depleted condition is shown in Fig. S5.

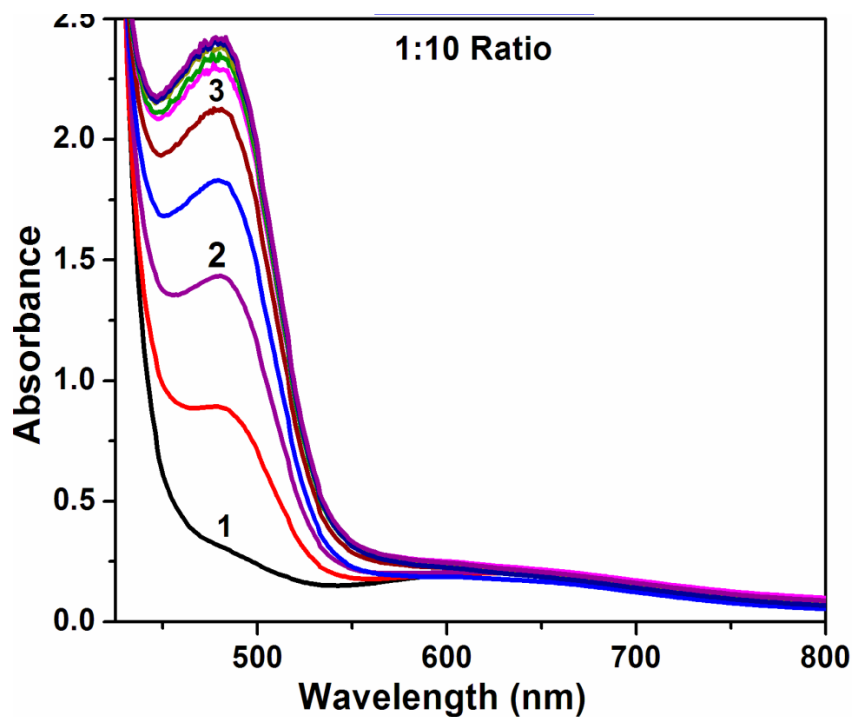


Figure S4. UV-Visible spectra of phen-dione using Complex [Cu(L)Cl] (**2**) in 1:10 ratio under aerobic condition. **1** = 2 mins; **2** = 50 mins; **3**= 100 mins

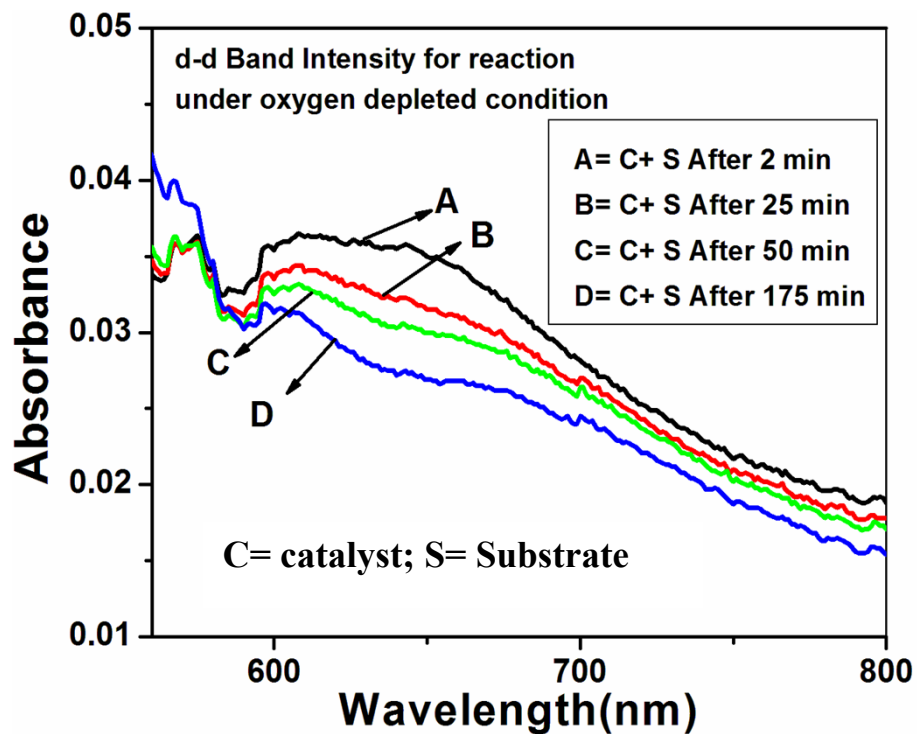


Figure S5. Loss in the d-d band intensity of complex (1) under oxygen depleted condition

Roll of H₂O₂

When the experiment is proceed in presnence of hydrogen peroxide we found that the rate is decreases when the oxidation is proceed in the raio of Catalyst: Substrate: H₂O₂ (1: 10: 1). When we have increase the percentage of H₂O₂ we found that rate get suppressed. This confirm that the H₂O₂ is released during the catalysis cycle.

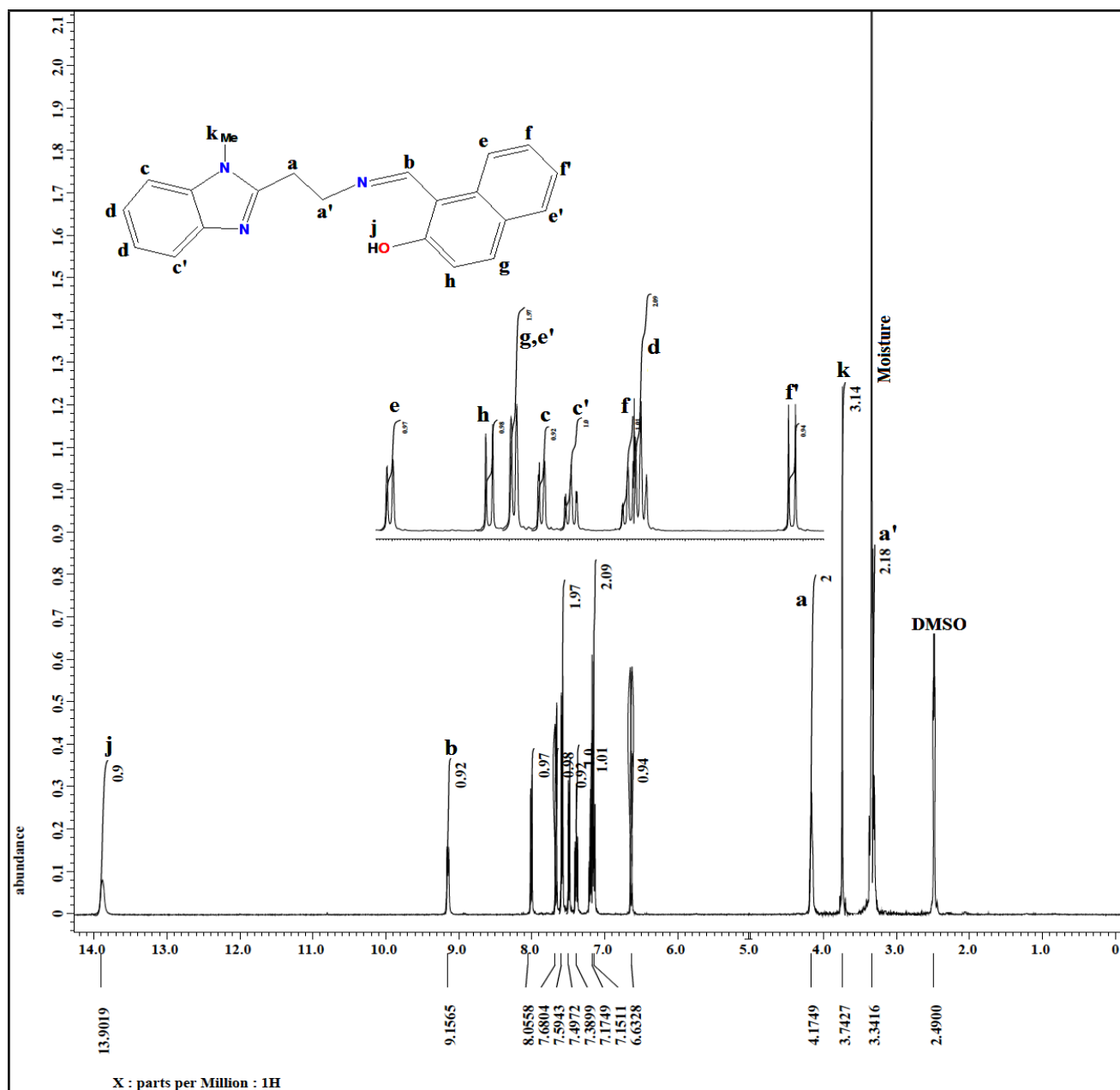


Figure S6. $^1\text{H-NMR}$ Spectra of ligand in $d^6\text{-DMSO}$. Inset shows magnification of aromatic region

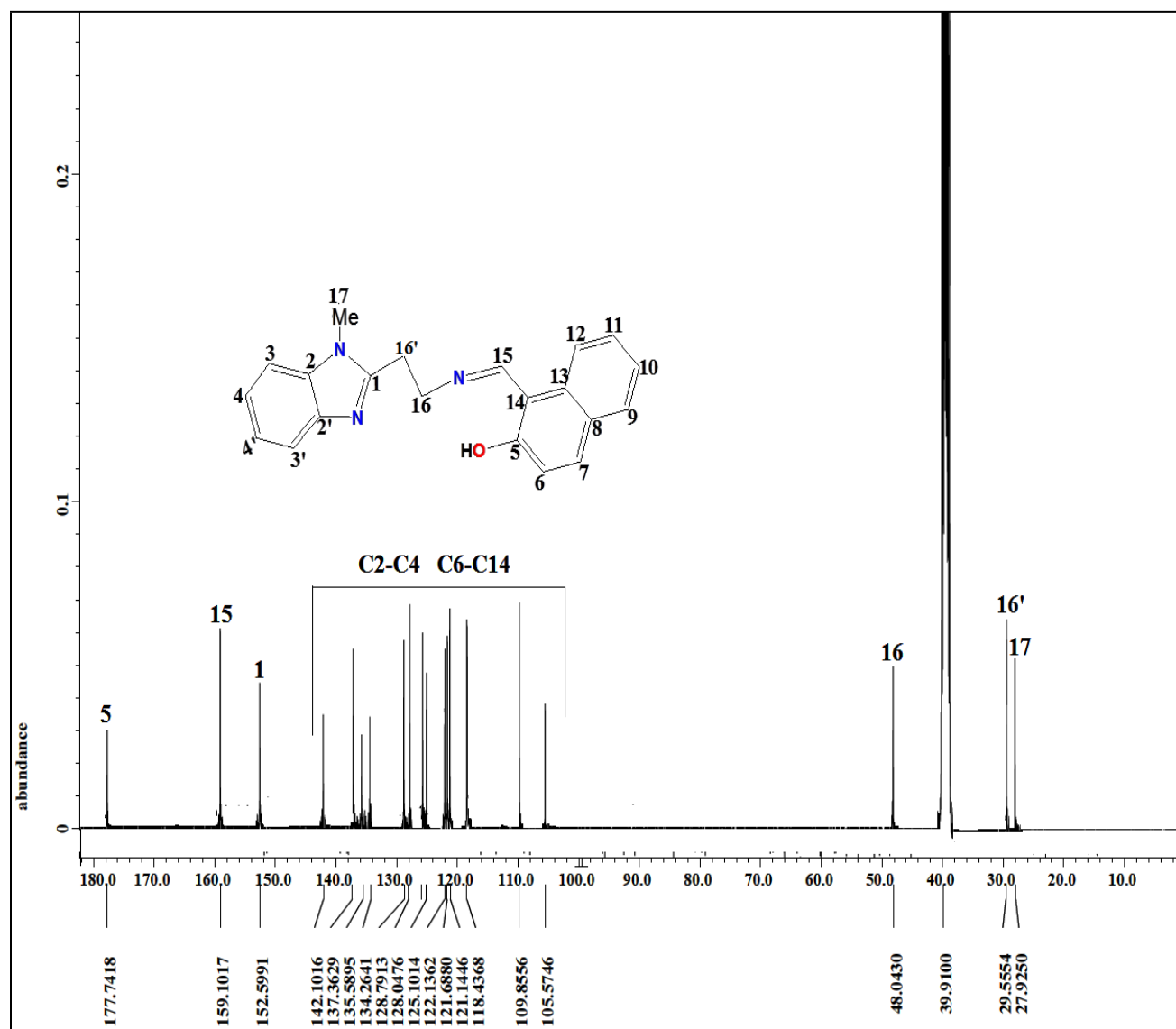


Figure S7. ¹³C-NMR Spectra of ligand in d⁶-DMSO.

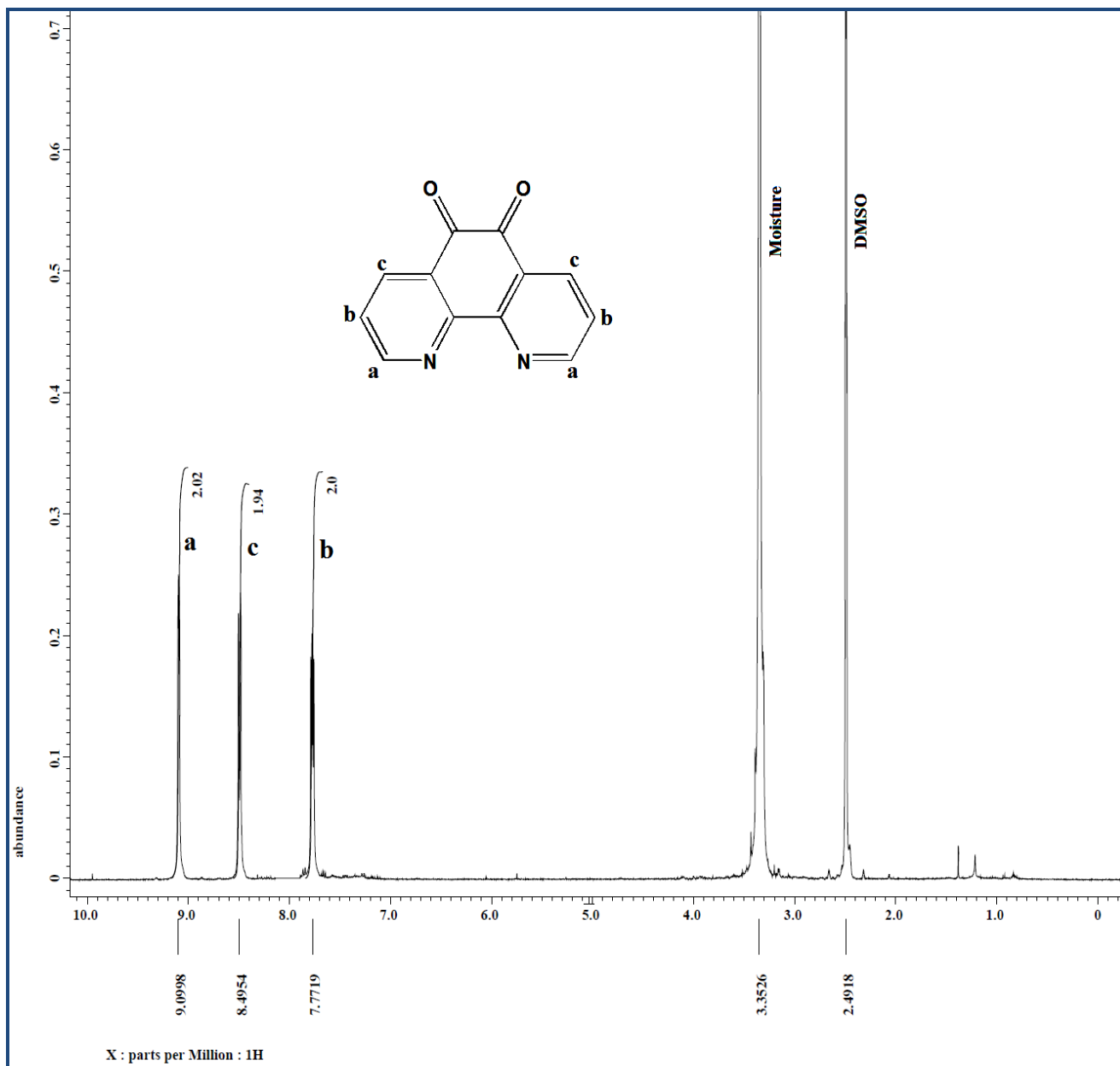


Figure S8. ¹H-NMR Spectra of 1,10-Phenanthroline 5,6-dione (Phen-dione) in d⁶-DMSO

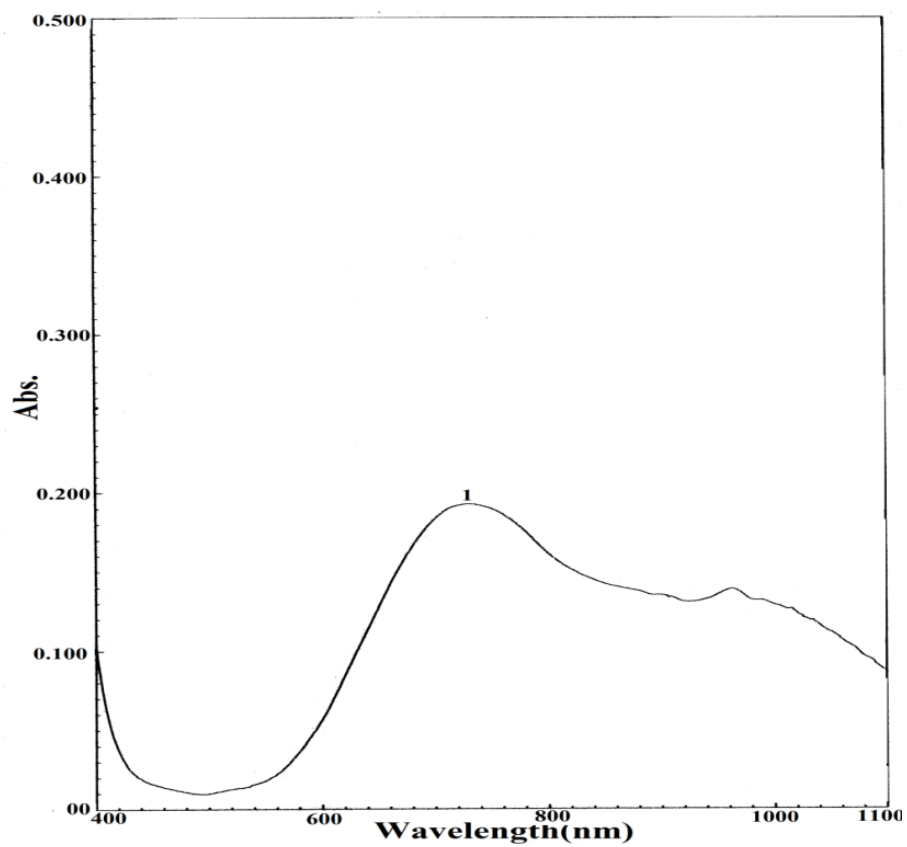


Figure S9. Spectra show formation of Cu-Phenanthroline complex at 732 nm in visible region

Table S1. Crystallographic Data and Structure Refinement of Ligand (HL) and its complex.

	Ligand	Complex (1)	Complex (2)
Empirical formula	$C_{21}H_{19}N_3O$	$C_{21}H_{18}CuN_4O_4$	$C_{21}H_{18}ClCuN_3O$
M	329.39	453.93	427.37
Temp.(K)	298(2)	150(2)	298(2) K
Wavelength/ Å	0.71073	0.71073	0.71073 Å
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P 21/c	P-1	<i>P 21/c</i>
a/ Å	13.5776(8)	8.1881(4)	<i>a</i> = 8.2057(6) Å
b/ Å	8.7158(5)	14.3725(7)	<i>b</i> = 23.5851(16) Å
c/ Å	15.1599(11)	16.7302(8)	<i>c</i> = 9.7520(9) Å
Volume/Å ³	1714.96(19)	1829.21(15)	1810.3(2)
Z	4	4	4
D _c / Mg/m ³	1.276	1.648	1.568
μ/mm ⁻¹	0.080	1.234	1.370
F(000)	696	932	876
R(int)	0.0218	0.0408	0.0559
Crystal size/mm ³	0.12 x 0.10 x 0.08	0.12×0.11×0.10	0.10 x 0.08 x 0.06
Reflections collected	13105	24033	15920
Independent reflections	3372	7164	3544
Goodness-of-fit on F ²	1.036	1.038	1.194
Final R1, wR2	0.0455, 0.1067	0.0304, 0.0745	0.0617, 0.1245
R indices (all data)	0.0591, 0.1134	0.0355, 0.0767	0.0772, 0.1302
Largest diff. peak and hole/ e.Å ⁻³	0.183 and -0.159	0.307 and -0.475	0.577 and -0.320

Table S2. Bond lengths [Å] and angles [°] for complexes (1) and (2).

Bond lengths (Å) for [Cu(L)NO₃] (1)

Interatom	Bond Length	Interatom	Bond Length
C(1)-C(2)	1.414(3)	C(27)-N(4)	1.378(3)
C(1)-C(6)	1.418(3)	C(28)-N(4)	1.461(3)
C(1)-C(10)	1.453(3)	C(29)-N(5)	1.332(3)
C(2)-C(3)	1.375(3)	C(29)-N(4)	1.352(3)
C(3)-C(4)	1.400(3)	C(29)-C(30)	1.495(3)
C(4)-C(5)	1.371(3)	C(30)-C(31)	1.523(3)
C(5)-C(6)	1.409(3)	C(31)-N(6)	1.466(3)
C(6)-C(7)	1.429(3)	C(32)-N(6)	1.296(3)
C(7)-C(8)	1.353(3)	C(32)-C(33)	1.427(3)
C(8)-C(9)	1.439(3)	C(33)-C(34)	1.412(3)
C(9)-O(1)	1.298(2)	C(33)-C(42)	1.451(3)
C(9)-C(10)	1.414(3)	C(34)-O(5)	1.302(3)
C(10)-C(11)	1.430(3)	C(34)-C(35)	1.433(3)
C(11)-N(3)	1.290(3)	C(35)-C(36)	1.352(3)
C(12)-N(3)	1.473(2)	C(36)-C(37)	1.419(3)
C(12)-C(13)	1.514(3)	C(37)-C(38)	1.407(3)
C(13)-C(14)	1.492(3)	C(37)-C(42)	1.424(3)
C(14)-N(2)	1.333(3)	C(38)-C(39)	1.366(4)
C(14)-N(1)	1.343(3)	C(39)-C(40)	1.397(3)
C(15)-N(1)	1.460(3)	C(40)-C(41)	1.374(3)
C(16)-N(1)	1.385(3)	C(41)-C(42)	1.406(3)
C(16)-C(17)	1.390(3)	N(2)-Cu(1)	1.9815(17)
C(16)-C(21)	1.399(3)	N(3)-Cu(1)	1.9374(17)
C(17)-C(18)	1.378(3)	N(5)-Cu(2)	1.9838(17)
C(18)-C(19)	1.396(3)	N(6)-Cu(2)	1.9247(17)
C(19)-C(20)	1.381(3)	N(7)-O(3)	1.231(2)
C(20)-C(21)	1.400(3)	N(7)-O(4)	1.247(2)
C(21)-N(2)	1.404(3)	N(7)-O(2)	1.285(2)
C(22)-C(23)	1.393(3)	N(8)-O(7)	1.228(2)
C(22)-C(27)	1.396(3)	N(8)-O(8)	1.246(2)
C(22)-N(5)	1.406(3)	N(8)-O(6)	1.280(2)

C(23)-C(24)	1.385(3)	O(1)-Cu(1)	1.8838(14)
C(24)-C(25)	1.398(3)	O(2)-Cu(1)	2.0253(15)
C(25)-C(26)	1.379(3)	O(5)-Cu(2)	1.8704(14)
C(26)-C(27)	1.392(3)	O(6)-Cu(2)	2.0318(15)

Bond Angles (Å) for [Cu(L)NO₃] (1)

Atoms	Angles	Atoms	Angles
C(2)-C(1)-C(6)	117.11(19)	O(5)-C(34)-C(35)	116.36(19)
C(2)-C(1)-C(10)	123.97(18)	C(33)-C(34)-C(35)	118.68(19)
C(6)-C(1)-C(10)	118.92(18)	C(36)-C(35)-C(34)	121.4(2)
C(3)-C(2)-C(1)	121.7(2)	C(35)-C(36)-C(37)	121.8(2)
C(2)-C(3)-C(4)	120.8(2)	C(38)-C(37)-C(36)	121.3(2)
C(5)-C(4)-C(3)	118.9(2)	C(38)-C(37)-C(42)	119.7(2)
C(4)-C(5)-C(6)	121.4(2)	C(36)-C(37)-C(42)	119.0(2)
C(5)-C(6)-C(1)	120.04(19)	C(39)-C(38)-C(37)	121.2(2)
C(5)-C(6)-C(7)	120.8(2)	C(38)-C(39)-C(40)	119.5(2)
C(1)-C(6)-C(7)	119.20(19)	C(41)-C(40)-C(39)	120.6(2)
C(8)-C(7)-C(6)	121.6(2)	C(40)-C(41)-C(42)	121.5(2)
C(7)-C(8)-C(9)	121.47(19)	C(41)-C(42)-C(37)	117.4(2)
O(1)-C(9)-C(10)	125.52(18)	C(41)-C(42)-C(33)	123.45(19)
O(1)-C(9)-C(8)	116.14(18)	C(37)-C(42)-C(33)	119.1(2)
C(10)-C(9)-C(8)	118.31(19)	C(14)-N(1)-C(16)	107.79(16)
C(9)-C(10)-C(11)	120.09(18)	C(14)-N(1)-C(15)	126.15(17)
C(9)-C(10)-C(1)	120.40(18)	C(16)-N(1)-C(15)	126.04(17)
C(11)-C(10)-C(1)	119.32(18)	C(14)-N(2)-C(21)	105.37(17)
N(3)-C(11)-C(10)	127.32(19)	C(14)-N(2)-Cu(1)	124.92(14)
N(3)-C(12)-C(13)	112.64(17)	C(21)-N(2)-Cu(1)	129.67(13)
C(14)-C(13)-C(12)	113.85(17)	C(11)-N(3)-C(12)	117.62(17)
N(2)-C(14)-N(1)	112.41(18)	C(11)-N(3)-Cu(1)	125.17(14)
N(2)-C(14)-C(13)	126.40(18)	C(12)-N(3)-Cu(1)	117.03(13)
N(1)-C(14)-C(13)	121.13(17)	C(29)-N(4)-C(27)	108.08(17)
N(1)-C(16)-C(17)	131.31(19)	C(29)-N(4)-C(28)	125.86(18)
N(1)-C(16)-C(21)	105.80(17)	C(27)-N(4)-C(28)	125.78(18)
C(17)-C(16)-C(21)	122.88(19)	C(29)-N(5)-C(22)	105.65(17)

C(18)-C(17)-C(16)	116.4(2)	C(29)-N(5)-Cu(2)	125.19(14)
C(17)-C(18)-C(19)	121.6(2)	C(22)-N(5)-Cu(2)	128.99(14)
C(20)-C(19)-C(18)	121.9(2)	C(32)-N(6)-C(31)	118.97(18)
C(19)-C(20)-C(21)	117.5(2)	C(32)-N(6)-Cu(2)	124.27(14)
C(16)-C(21)-C(20)	119.71(19)	C(31)-N(6)-Cu(2)	116.71(14)
C(16)-C(21)-N(2)	108.62(17)	O(3)-N(7)-O(4)	122.8(2)
C(20)-C(21)-N(2)	131.65(19)	O(3)-N(7)-O(2)	119.24(19)
C(23)-C(22)-C(27)	120.39(19)	O(4)-N(7)-O(2)	117.98(18)
C(23)-C(22)-N(5)	130.96(19)	O(7)-N(8)-O(8)	122.87(19)
C(27)-C(22)-N(5)	108.56(18)	O(7)-N(8)-O(6)	119.21(18)
C(24)-C(23)-C(22)	117.4(2)	O(8)-N(8)-O(6)	117.92(18)
C(23)-C(24)-C(25)	121.5(2)	C(9)-O(1)-Cu(1)	128.24(13)
C(26)-C(25)-C(24)	121.8(2)	N(7)-O(2)-Cu(1)	105.42(12)
C(25)-C(26)-C(27)	116.5(2)	C(34)-O(5)-Cu(2)	125.20(13)
N(4)-C(27)-C(26)	131.59(19)	N(8)-O(6)-Cu(2)	106.59(12)
N(4)-C(27)-C(22)	105.96(18)	O(1)-Cu(1)-N(3)	92.51(7)
C(26)-C(27)-C(22)	122.4(2)	O(1)-Cu(1)-N(2)	161.02(7)
N(5)-C(29)-N(4)	111.73(18)	N(3)-Cu(1)-N(2)	94.47(7)
N(5)-C(29)-C(30)	126.05(19)	O(1)-Cu(1)-O(2)	86.88(6)
N(4)-C(29)-C(30)	122.15(18)	N(3)-Cu(1)-O(2)	155.78(7)
C(29)-C(30)-C(31)	115.00(18)	N(2)-Cu(1)-O(2)	93.82(6)
N(6)-C(31)-C(30)	111.41(17)	O(5)-Cu(2)-N(6)	93.11(7)
N(6)-C(32)-C(33)	125.68(19)	O(5)-Cu(2)-N(5)	159.63(7)
C(34)-C(33)-C(32)	120.94(19)	N(6)-Cu(2)-N(5)	93.58(7)
C(34)-C(33)-C(42)	119.90(18)	O(5)-Cu(2)-O(6)	88.50(6)
C(32)-C(33)-C(42)	119.08(19)	N(6)-Cu(2)-O(6)	157.44(7)
O(5)-C(34)-C(33)	124.94(19)	N(5)-Cu(2)-O(6)	92.63(7)

Bond lengths (Å) for [Cu(L)Cl] (2)

Interatom	Bond Length	Interatom	Bond Length
C(1)-N(2)	1.391(6)	C(12)-C(21)	1.408(6)
C(1)-C(2)	1.393(7)	C(12)-C(13)	1.430(6)
C(1)-C(6)	1.403(6)	C(13)-C(14)	1.410(6)
C(2)-C(3)	1.380(7)	C(13)-C(18)	1.411(6)

C(3)-C(4)	1.393(8)	C(14)-C(15)	1.366(6)
C(4)-C(5)	1.380(8)	C(15)-C(16)	1.400(7)
C(5)-C(6)	1.381(7)	C(16)-C(17)	1.353(7)
C(6)-N(1)	1.383(6)	C(17)-C(18)	1.413(6)
C(7)-N(1)	1.467(6)	C(18)-C(19)	1.425(7)
C(8)-N(2)	1.325(6)	C(19)-C(20)	1.343(7)
C(8)-N(1)	1.347(6)	C(20)-C(21)	1.438(6)
C(8)-C(9)	1.475(6)	C(21)-O(1)	1.297(5)
C(9)-C(10)	1.515(6)	N(2)-Cu(1)	1.978(4)
C(10)-N(3)	1.474(6)	N(3)-Cu(1)	1.972(4)
C(11)-N(3)	1.283(5)	O(1)-Cu(1)	1.907(3)
C(11)-C(12)	1.432(6)	Cl(1)-Cu(1)	2.2414(13)

Bond Angles (Å) for [Cu(L)Cl] (2)

Atoms	Angles	Atoms	Angles
N(2)-C(1)-C(2)	132.1(4)	C(16)-C(17)-C(18)	120.9(5)
N(2)-C(1)-C(6)	108.2(4)	C(13)-C(18)-C(17)	120.3(4)
C(2)-C(1)-C(6)	119.7(4)	C(13)-C(18)-C(19)	117.8(4)
C(3)-C(2)-C(1)	117.6(5)	C(17)-C(18)-C(19)	121.9(4)
C(2)-C(3)-C(4)	121.6(5)	C(20)-C(19)-C(18)	122.8(4)
C(5)-C(4)-C(3)	121.8(5)	C(19)-C(20)-C(21)	120.8(4)
C(4)-C(5)-C(6)	116.3(5)	O(1)-C(21)-C(12)	124.5(4)
C(5)-C(6)-N(1)	131.3(5)	O(1)-C(21)-C(20)	117.6(4)
C(5)-C(6)-C(1)	123.0(5)	C(12)-C(21)-C(20)	117.9(4)
N(1)-C(6)-C(1)	105.7(4)	C(8)-N(1)-C(6)	107.8(4)
N(2)-C(8)-N(1)	111.8(4)	C(8)-N(1)-C(7)	127.1(4)
N(2)-C(8)-C(9)	124.2(4)	C(6)-N(1)-C(7)	125.0(4)
N(1)-C(8)-C(9)	124.1(4)	C(8)-N(2)-C(1)	106.5(4)
C(8)-C(9)-C(10)	112.5(4)	C(8)-N(2)-Cu(1)	124.5(3)
N(3)-C(10)-C(9)	112.9(4)	C(1)-N(2)-Cu(1)	129.0(3)
N(3)-C(11)-C(12)	127.5(4)	C(11)-N(3)-C(10)	116.9(4)
C(21)-C(12)-C(13)	120.8(4)	C(11)-N(3)-Cu(1)	121.9(3)
C(21)-C(12)-C(11)	119.4(4)	C(10)-N(3)-Cu(1)	121.2(3)
C(13)-C(12)-C(11)	119.3(4)	C(21)-O(1)-Cu(1)	125.1(3)

C(14)-C(13)-C(18)	116.7(4)	O(1)-Cu(1)-N(3)	90.21(14)
C(14)-C(13)-C(12)	123.6(4)	O(1)-Cu(1)-N(2)	154.51(15)
C(18)-C(13)-C(12)	119.7(4)	N(3)-Cu(1)-N(2)	93.96(15)
C(15)-C(14)-C(13)	122.2(5)	O(1)-Cu(1)-Cl(1)	93.19(11)
C(14)-C(15)-C(16)	120.1(5)	N(3)-Cu(1)-Cl(1)	149.26(12)
C(17)-C(16)-C(15)	119.7(5)	N(2)-Cu(1)-Cl(1)	95.91(11)

Symmetry transformations used to generate equivalent atoms

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