RSC Advances



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PAPER



Cite this: RSC Adv., 2015, 5, 643

C-Nitrosation of a β-diketiminate ligand in copper(II) complex†

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A copper(II) complex, **1** of a β -diketiminate ligand {L = (4-(2,6-dimethylphenylimino)pentane-2ylidene)-2,6dimethylbenzeneamine} has been synthesized and characterized. Single crystal X-ray structure reveals the presence of a mononuclear copper(II) unit with a distorted square planar geometry. In acetonitrile solution of the complex, the β -diketiminate ligand undergoes oxidative degradation to the corresponding ketone diimine under aerobic condition. Addition of nitric oxide to the acetonitrile solution of complex **1** affords the corresponding oxime diimine ligand. All the modified ligands have been isolated and characterized.

Introduction

Received 7th August 2014

DOI: 10 1039/c4ra08281h

www.rsc.org/advances

Accepted 21st November 2014

 β -Diketiminate derivatives with bulky aromatic groups as Nsubstituents have attracted considerable research interest from coordination chemists.¹⁻³ These mono-anionic bidentate ligands are isoelectronic to cyclopentadienyl anions; their steric and electronic properties can easily be altered by switching to appropriate amine and diketone derivatives for synthesis.^{4,5} They afford coordinatively unsaturated and stable mono-/ binuclear complexes of transition and lanthanide metal ions.^{6,7} These complexes find extensive applications as catalysts as well as models for active sites of metallo-enzymes.⁸⁻¹⁰

In general β-diketiminate frameworks are obtained from the reaction of acetylacetone with appropriate aniline derivative. They are stable and allow the synthesis and characterization of a wide range of metal complexes.11 However, examples of ligand modification during catalysis reactions are also known in some cases.^{12,13} Itoh and coworkers demonstrated that β -diketiminate ligand with mesityl substituents at N-atom in copper(II) complex in methanol solution undergoes easy oxidative transformation to the corresponding keto-diimine under aerobic condition.¹⁴ When the reaction mixture was allowed to stand for few days, the crystals of copper(II) complex of the corresponding hemiacetal derivative of the ketone diimine were obtained. However, the demetallation of this complex was reported to afford the corresponding ketone diimine. The similar reaction was reported with complex of Zn(II), also.¹⁵ In anaerobic condition, the reaction did not occur. The labelling experiment with ¹⁸O₂ confirmed the involvement of molecular oxygen. The reaction was proposed to proceed through the formation of bridged



Fig. 1 Ligand, L, used for the present study

peroxo intermediate.¹⁴ In spite, there has not been much study on the degradation of β -diketiminate ligand frameworks in presence of metal ions.

This reaction instigates to study the reactivity of copper(π) complex of a β -diketiminate ligand, (L), with molecular oxygen and nitric oxide (NO) (Fig. 1). The ligand undergoes oxidative degradation to the corresponding ketone diimine (L1) in case of reaction with molecular oxygen and *C*-nitrosation during reaction with NO to afford corresponding oxime di-imine framework, L2.

Results and discussion

The ligand L was prepared by reacting acetylacetone with 2,6dimethyl aniline using a reported procedure.¹⁵ The copper(π) complex, **1** used for the present study was prepared by stirring the free ligand with equivalent amount of copper(π) acetate in acetonitrile at room temperature. Complex **1** was characterized by various spectroscopic techniques as well as by single crystal structure determination. The ORTEP diagram is shown in Fig. 2. The crystal structure reveals the mononuclear metal center with a distorted square planar geometry where the anionic β -diketiminate and acetate act as bidentate ligands. The crystallographic data, important bond angles and distances are listed in Tables 1–3, respectively. The average Cu–N distance is 1.900 (3) Å. C–N and C–C distances of the diketiminate

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T Electronic supplementary information (ESI) available: The detail experimental processes and all characterization data are included. CCDC 1006415, 1007056 and 1006417. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ra08281h



Fig. 2 ORTEP diagram of complex 1 (50% thermal ellipsoid plot; Hatoms are removed for clarity).

framework are 1.340(4) Å and 1.387 Å, respectively. Average Cu–O_{acetate} distance is 2.018 Å. In acetate, the C–O distance is 1.255 Å. The bite angle of the diketiminate ligand is 96.30°; whereas for acetate, this is 64.22°. For copper(II) complex of the β -diketiminate ligand having mesityl substituents at N atom, the average Cu–N and Cu–O distances are 1.915 and 2.028 Å, respectively.¹⁴

Complex 1 in acetonitrile solution displays d–d transitions at 772 nm and 559 nm in the visible spectrum (Fig. 3) along with

intra-ligand transitions in UV-range. In X-band EPR spectra, complex **1** exhibits four line spectrum characteristics to the square planar copper(π) complexes with $d_{x^2-y^2}$ ground state (Fig. 4).¹⁶

The colour of the acetonitrile solution of complex **1** changed to green when heated to 50 °C for 2 h under aerobic condition. This led to the oxidation of the ligand to corresponding ketone diimine analogue, **L1**. Similar observation was reported earlier by Itoh *et al.*¹⁴ The reaction presumably proceeds through the formation of a bridged peroxo intermediate as proposed by Itoh *et al.* (Scheme 1).¹⁴ The modified ketone diimine ligand, **L1** was isolated quantitatively from the reaction mixture after removal of copper(II) ion using aqueous Na₂S (experimental section). **L1** was characterized using various spectral analyses. We could not grow the X-ray quality crystals of it. However, when the crude reaction mixture was kept at room temperature, dark green crystals of complex **2** appeared (ESI[†]).

The ORTEP diagram of complex 2 is shown in Fig. 5b. The crystal data and bond angle and distances are shown in Tables 1–3, respectively. The crystal structure reveals the heptanuclear structure of complex 2 and the formation of corresponding diol diimine which actually dehydrates while demetallated to afford the ketone diimine. PLATON/SQUEEZE was performed to refine the framework for complex 2 along with the water molecules in the crystal by excluding the disordered solvent electron

Table 1 Crystallographic data for complex 1, complex 2 and L2

	Complex 1	Complex 2	L2
Formulas	C23H28Cu1N2O2	C77H129Cu7N7O38	$C_{21}H_{25}N_3O_1$
Mol. wt.	428.01	2205.65	335.44
Crystal system	Triclinic	Cubic	Mononclinic
Space group	$P\bar{1}$	P2 ₁ 3	I2/c
Temperature/K	296(2)	296(2)	296(2)
Wavelength/Å	0.71073	0.71073	0.71073
a/Å	7.0615(3)	22.7589(3)	21.2119(14)
<i>b</i> /Å	12.4388(6)	22.7589(3)	7.8518(4)
c/Å	13.4851(8)	22.7589(3)	23.5414(15)
α/deg	70.511(5)	90.00	90.00
β/deg	83.469(4)	90.00	95.420(6)
γ/deg	76.344(4)	90.00	90.00
$V/\text{\AA}^{-3}$	1084.26(10)	11788.3(2)	3903.3(4)
Ζ	2	4	8
Density/mg m^{-3}	1.311	1.243	1.142
Abs. coeff/mm ⁻¹	1.027	1.310	0.071
Abs. correction	Multi-scan	Multi-scan	None
<i>F</i> (000)	450	4588	1440
Total no. of reflections	3822	6992	3442
Reflections, $I > 2\sigma(I)$	3330	5668	2194
Max. $2\theta/\text{deg}$	25.00	25.24	25.00
Ranges (h, k, l)	$-8 \le h \le 8$	$-14 \le h \le 21$	$-24 \le h \le 25$
	$-14 \le k \le 8$	$-10 \le k \le 27$	$-9 \le k \le 9$
	$-16 \le l \le 15$	$-18 \le l \le 22$	$-27 \le l \le 27$
Complete to 2θ (%)	99.9	99.7	99.8
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
GoF (F^2)	0.966	1.065	1.011
<i>R</i> indices $[I > 2\sigma(I)]$	0.0478	0.0648	0.0573
R indices (all data)	0.1357	0.1303	0.1615
Flack parameter	_	-0.010(19)	



Fig. 3 UV-visible spectrum of complex 1 in acetonitrile.



Fig. 4 X-band EPR spectrum of complex 1 in acetonitrile at 77 K.

densities.17 These calculations amount to 601 electrons may be attributed to the water molecules.

This oxidative transformation is similar to what Itoh et al. reported earlier with mesityl substuted β-diketiminate. The crystal structure of the copper(II) complex with intermediate hemiacetal of the corresponding diketiminate was reported





Fig. 5 (a) Complex 2 and (b) ORTEP diagram of complex 2 (50% thermal ellipsoid plot; H-atoms and solvent molecules are removed for clarity).

from methanol solution. Demetallation of this complex using aqueous ammonia afforded the ketone diimine. A similar ligand oxygenation reaction was reported in Co(II) complexes of tetraaza macrocyclic dibenzotetramethyltetraaza-[14]annulene dianion.18

Addition of nitric oxide to the degassed acetonitrile solution of complex 1 resulted in colour change from brown to deep green through a transient intermediate step. The absorptions



Scheme 1

Table 2 Selected bond length (Å) of complex 1, complex 2 and L2

Complex 1	Bond length (Å)	Complex 2	Bond length (Å)	L2	Bond length (Å)
Cu1-O2	2.015(2)	Cu2-O5	2.102(3)	01-H1	0.819(2)
Cu1-O1	2.022(2)	Cu2-O6	2.108(4)	O1-N3	1.381(3)
Cu1-N1	1.899(3)	Cu1-O5	1.937(3)	N1-C9	1.267(3)
Cu1-N2	1.910(3)	Cu1-N1	2.001(4)	N1-C8	1.442(3)
O2-C22	1.254(5)	Cu1-O4	2.009(2)	N2-C12	1.281(3)
O1-C22	1.257(4)	Cu1-O2	1.964(4)	N2-C14	1.426(3)
N1-C8	1.443(5)	Cu1-O3	2.326(4)	N3-C11	1.279(3)
N1-C9	1.340(4)	Cu3-O6	1.945(3)	C9-C11	1.502(3)
N2-C14	1.434(3)	Cu3-N2	1.993(4)	C9-C10	1.492(4)
N2-C12	1.336(4)	Cu3-O7	1.977(2)	C11-C12	1.477(3)
C11-C12	1.394(5)	Cu3-O8	2.345(6)	C12-C13	1.495(4)

559 nm and 772 nm were diminished and a new band at 580 nm appeared (Fig. 6) for a short while suggesting the formation of the transient intermediate. This is presumably due to the formation of Cu(π)-nitrosyl intermediate. The frozen reaction mixture appeared silent in X-band EPR as expected for a Cu(π)-nitrosyl intermediate. FT-IR spectrum of the intermediate could not be recorded owing to its very less stability. The 580 nm absorption band diminished within few seconds and resulted in the appearance of an absorption band at 640 nm (Fig. 6) which is attributed to the d-d transition of copper(π) complex of modified oxime dimine ligand, **3**.

Complex 3 has been isolated as solid and characterized (experimental section and ESI[†]).

In FT-IR spectroscopy, complex 3 exhibits new stretching frequency at $\sim 1627 \text{ cm}^{-1}$. This band is assigned as the coordinated oxime stretching frequency (ESI[†]).¹⁹

Removal of copper(π) ion from the solution of complex 3 afforded the corresponding modified oxime diimine ligand, L2. The formation of L2 has been confirmed by various spectral analyses as well as by X-ray single crystal structure determination. The ORTEP diagram of L2 is shown in Fig. 7.



Fig. 6 UV-visible spectra of complex 1 before (black trace) and after (red trace) purging NO in acetonitrile. Blue represents the final compound (complex 3).



Fig. 7 ORTEP diagram of the oxime diimine, **L2** (50% thermal ellipsoid plot; H-atoms are removed for clarity).

Crystallographic data, important bond distances and angles are listed in Tables 1–3, respectively. The C–N_{imine} distances are 1.267(3) and 1.281(3) Å. C–N_{oxime} distance is 1.279(3) Å and N–O_{oxime} is 1.381(3) Å.

It should be noted that *C*-nitrosation did not occur while nitric oxide is purged to the acetonitrile solution of the free ligand. On the other hand, addition of NOClO₄ in the acetonitrile solution of **L** in presence of NaOEt, afforded corresponding *C*-nitrosation. Thus, the formation of copper(π)-nitrosyl with an electrophilic nitrosyl centre is the key step for the *C*-nitrosation reaction.

Though the detail mechanism of the *C*-nitrosation in the present case is not yet fully understood, presumably NO first binds to the metal center to form Cu(n)-nitrosyl intermediate as indicated by UV-visible and EPR studies. In the next step, nucleophillic attack to N-atom of NO by the diketiminate ligand

Table 3 Selected bond angles (°) of complex 1, complex 2 and L2

Complex 1	Bond angles (°)	Complex 2	Bond angles (°)	L2	Bond angles (°)
O2-Cu1-O1	64.2(1)	O6-Cu2-O5	154.6(1)	H1-O1-N3	109.5(2)
O2-Cu1-N1	164.0(1)	O5-Cu2-O6	65.8(1)	C9-N1-C8	120.6(2)
O2-Cu1-N2	99.7(1)	O5-Cu1-N1	82.7(2)	C12-N2-C14	120.3(2)
O1-Cu1-N1	99.7(1)	O5-Cu1-O4	92.1(1)	O1-N3-C11	112.4(2)
O1-Cu1-N2	163.8(1)	O5-Cu1-O2	170.1(2)	N1-C9-C11	117.1(2)
N1- Cu1-N2	96.3(1)	O5-Cu1-O3	94.6(2)	N1-C9-C10	126.7(2)
Cu1-O2-C22	89.3(2)	N1-Cu1-O4	158.7(1)	N3-C11-C9	124.4(2)
Cu1-O1-C22	89.0(2)	N1-Cu1-O2	93.0(2)	N3-C11-C12	117.2(2)
Cu1-N1-C8	116.7(2)	N1-Cu1-O3	103.0(2)	N2-C12-C11	115.4(2)
Cu1-N1-C9	123.8(2)	O4-Cu1-O2	88.8(1)	N2-C12-C13	125.8(2)
C8-N1-C9	119.5(3)	O4-Cu1-O3	98.0(1)	N1-C8-C6	121.4(2)
Cu1-N2-C14	116.9(2)	O2-Cu1-O3	95.0(2)	N1-C8-C2	116.8(2)
Cu1-N2-C12	123.4(2)	Cu2-O6-Cu3	108.8(2)	N2-C14-C20	119.7(2)
C14-N2-C12	119.7(2)	Cu2-O5-Cu1	110.3(2)	N2-C14-C15	118.6(2)
_	_	O6-Cu3-N2	82.9(2)	_	_
_	_	O6-Cu3-O7	93.0(1)	_	_
_	_	O6-Cu3-O9	172.5(2)	_	_
_	_	O6-Cu3-O8	92.7(2)	_	_
_	_	N2-Cu3-O7	164.3(2)	_	_
_	_	N2-Cu3-O9	91.9(2)	_	_
_	_	N2-Cu3-O8	104.6(2)	_	_
_	_	O7-Cu3-O9	90.6(2)	_	_
_	_	O7-Cu3-O8	90.7(2)	_	_
_	_	O9-Cu3-O8	94.0(2)	_	_
_	_	O4-Cu1-O5	92.1(1)	_	_
_	_	O4-Cu1-N1	158.7(1)	—	

takes place with successive loss of proton resulting to the oxime diimine moiety.

Experimental procedures

Materials and methods

All reagents and solvents were purchased from commercial sources and were of reagent grade. Acetonitrile was distilled from calcium hydride. Deoxygenation of the solvent and solutions were effected by repeated vacuum/purge cycles or bubbling with Ar for 30 minutes. NO gas was purified by passing through KOH and P2O5 column. UV-visible spectra were recorded on a Perkin Elmer lamda 25 UV-visible spectrophotometer. FT-IR spectra were taken on a Perkin Elmer spectrophotometer with either sample prepared as KBr pellets or in solution in a sodium chloride cell. Solution electrical conductivity was checked using a Systronic 305 conductivity bridge. ¹H-NMR spectra were obtained with a 400 MHz Varian FTspectrometer. Chemical shifts (ppm) were referenced either with an internal standard (Me₄Si) for organic compounds or to the residual solvent peaks. The X-band Electron Paramagnetic Resonance (EPR) spectra of the complexes and of the reaction mixtures were recorded on a JES-FA200 ESR spectrometer with frequency, 9431.848 MHz; center field, 336.0 mT; power, 0.998 mW; modulation width, 0.80 mT; time constant, 0.03 s and sweep time, 30.0 s.

Elemental analyses were obtained from a Perkin Elmer Series II Analyzer. The magnetic moment of complexes are measured on a Cambridge Magnetic Balance. Single crystals were grown by slow diffusion followed by slow evaporation technique. The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube MoK α radiation ($\lambda = 0.71073$ Å) at 273(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s per frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP software.²⁰ Multi-scan empirical absorption corrections were applied to the data using the program SADABS.²¹ Structures were solved by direct methods using SHELXS-97 and refined with full-matrix least squares on F^2 using SHELXL-97.²² All non-hydrogen atoms were refined anisotropically. Structural illustrations have been drawn with ORTEP-3 for Windows.²³

Synthesis

Synthesis of ligand L. The ligand L was synthesized by a reported procedure.¹⁵ A mixture of 20.3 ml 2,6-dimethylaniline (20 g, 0.17 mol), 8.5 ml 2,4-pentanedione (8.25 g, 0.08 mol) and 14.2 g *p*-toluenesulphonic acid in 250 ml of dry toluene was refluxed for 24 h. The toluene was decanted, and to the solid residue 200 ml diethyl ether was added followed by 150 ml water and 36 g Na₂CO₃·10H₂O. After stirring for 25 min, the ether layer was separated, dried with MgSO₄, and the solvent was removed in vacuum. The residue was dried in vacuum at 100 °C for 6 h to remove any remaining free 2,6-dimethylaniline, giving crystalline solid of L. Yield: 18.8 g (74%). FT-IR: 3009, 2918, 2852, 1625, 1551, 1487, 1465, 1432, 1376, 1278, 1181, 1090, 1024, 767 cm⁻¹. ¹H-NMR: (600 MHz, CDCl₃): δ_{ppm} : 1.80 (6H, s),

2.28 (12H, s), 4.99 (1H, s), 7.04–7.06 (2H, t), 7.13–7.15 (4H, d), 12.32 (1H, s). $^{13}\text{C-NMR}$: (150 MHz, CDCl₃): δ_{ppm} : 18.5, 20.4, 93.6, 124.4, 127.9, 132.2, 143.9, 160.9.

Synthesis of complex 1. $Cu^{II}(CH_3COO)_2 \cdot 2H_2O$ (0.997 g, 5 mmol) was dissolved in 10 ml of acetonitrile. Chloroform solution (10 ml) of L (1.53 g, 5 mmol) was added slowly with constant stirring. The colour of the solution turned to brown from green. The stirring was continued for 2 h at room temperature. The solution was dried in rotary evaporator to obtain a brown solid. The solid was then washed with distilled water and dried to get crystalline solid of complex 1. Yield: 2.02 g (80%). UV-vis (acetonitrile): λ_{max} (ε , M⁻¹ cm⁻¹): 772 nm (55) 559 nm (160), λ_{max} , 359 nm (2105). X-band EPR (in acetonitrile at 77 K): g_{||}, 2.189; g_{\perp}, 2.056. FT-IR (KBr pellet): 3016, 2975, 2919, 1556, 1529, 1470, 1393, 1261, 1182, 1024, 945, 859, 761, 692, 609 cm⁻¹. Complex 1 behaves as non-electrolyte in acetonitrile solution. The observed magnetic moment is 1.57 BM.

Synthesis of complex 2. Complex 1 (100 mg) was dissolved in 20 ml acetonitrile in a round bottom flask. The solution was heated to 50 °C with constant stirring for 2 h under aerobic condition. The colour of the solution changed to dark green. The reaction mixture was cooled to room temperature and allowed to stand for 24 h to obtain green crystals of complex 2. The crystals were filtered out and characterized. Yield, 53 mg (~80%). UV-visible (acetonitrile): λ_{max} (ε , M⁻¹ cm⁻¹): 725 nm (158), 241 nm (4473). FT-IR (KBr pellet): 3419, 2921, 1647, 1590, 1469, 1440, 1204, 1092, 1036, 766 cm⁻¹.

Synthesis of complex 3. To a degassed acetonitrile (10 ml) solution of complex 1 (100 mg), nitric oxide was purged till the colour of the solution changed to deep green from light brown. The solution was allowed to stand at room temperature for 1/2 h. The excess nitric oxide was removed by applying several cycles of vacuum followed by purging Ar. The volume of the solution was reduced to 2 ml and benzene (10 ml) was added to make a layer and kept in freezer for overnight. The complex 3 was obtained as green precipitate. It was filtered off and washed with diethylether. Yield, 80 mg (~74%). UV-visible (acetonitrile): λ_{max} (ε , M⁻¹ cm⁻¹): 640 nm (189), 246 nm (2643). FT-IR: 3444, 2921, 1627, 1566, 1470, 1439, 1335, 1198, 1094, 768 cm⁻¹.

Isolation of ligand L1. Complex 1 (300 mg) was dissolved in 20 ml acetonitrile in a round bottom flask. The solution was heated to 50 °C with constant stirring for 2 h under aerobic condition while the colour of the solution changed to dark green. After cooling down to room temperature, the volume of the solution was reduced to 2 ml. To this, 5 ml saturated aqueous solution of Na₂S was added with constant stirring for 1/ 2 h. The black precipitate thus appeared was filtered off and the filtrate was diluted with 25 ml water. Then the organic part was extracted with chloroform (20 ml \times 3 portions). The combined chloroform layer was dried and subjected to column chromatography to get L1. Yield, 135 mg (~60%). FT-IR: 3419, 2922, 1705, 1675, 1593, 1471, 1440, 1366, 1208, 110, 1092, 764 cm⁻¹. ¹H-NMR: (400 MHz, CDCl₃): δ_{ppm} : 1.94 (6H, s), 2.02 (12H, s), 5.00 (1H, s), 6.92-6.95 (2H, t), 7.01-7.05 (4H, d). ESI-Mass (M + 1): calcd: 321.1889; found: 321.1934.

Isolation of modified ligand, L2. Complex **1** (300 mg) was dissolved in acetonitrile (10 ml). To this nitric oxide gas was

purged till the colour of the solution changed to deep green. The solution was allowed to stand for 1/2 h. The excess NO was removed by applying vacuum and purging Ar. The volume of the solution was reduced to ~ 1 ml. To this saturated aqueous solution of Na₂S was added and the mixture was stirred for 1/2 h. The black precipitate thus appeared was filtered out. To the filtrate 20 ml of water was added. Few drops of acetic acid were added to neutralize the solution and then the organic part was extracted with chloroform (3 portions \times 25 ml). Extracted organic portion was dried under vacuum and pure L2 was obtained. Yield, 52 mg (~65%). FT-IR (in KBr) 3144, 3017, 2852, 1666, 1625, 1591, 1470, 1368, 1337, 1206, 1092, 1069, 1001, 830, 817, 771, 764 cm⁻¹. ¹H-NMR: (600 MHz, CDCl₃): δ_{ppm}: 1.92 (3H, s), 1.96 (3H, s), 2.01 (6H, s), 2.13 (6H, s), 6.90-6.95 (2H, m), 7.02-7.04 (4H, t), 10.93 (1H, s). ¹³C-NMR: (150 MHz, CDCl₃): δ_{ppm} : 16.2, 18.1, 18.5, 20.7, 123.3, 124.1, 125.2, 128.0, 164.6. The X-ray quality single crystals were grown from the chloroform solution of the modified ligand, L2.

Conclusion

In the copper(π) complex, the β -diketiminate ligand, L undergoes oxidative degradation in acetonitrile solution under aerobic condition to afford corresponding ketone diimine. The reaction possibly proceeds through a peroxo intermediate. On the other hand, addition of nitric oxide to the acetonitrle solution of complex 1 results in the *C*-nitrosation of the ligand framework and affords corresponding oxime diimine. The modified ligands are isolated and characterized. The formation of the oxime diimine is further supported by X-ray single crystal structure determination. The reaction, presumably, proceeds through the formation of copper(π)-nitrosyl intermediate.

Acknowledgements

The authors sincerely thank the Department of Science and Technology, India for financial support; DST-FIST for X-ray diffraction facility. AK and VK would like to thank CSIR, India for providing the scholarship.

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