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Copper(II) acetate mediated conversion of *ortho* aminomethyl substituted isoquinolines to bis(isoquinolylcarbonyl)amides

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ABSTRACT

An ethanolic solution of *ortho* aminomethyl substituted isoquinolines, on stirring in air with half equivalent of $[Cu(OAc)_2(H_2O)]$, afforded [Cu(**1-L**)(OAc)] (**1**) and [Cu(**3-L**)(OAc)] (**2**) {**1-L** = bis(1-isoquinolylcarbonyl)amide ion and **3-L** = bis(3-isoquinolylcarbonyl)amide ion}. This reaction involves the oxidation of a methylene group and the formation of a bond between nitrogen and carbon in N–C(=O) through coupling. The free ligands can be isolated as crystalline solids from compounds **1**–**2**, by extrusion of the Cu^{2+} ion using $EDTA^{2-}$. The molecular structure of **1**·$2.5H_2O$ has been established and the copper(II) center has a pseudo square-planar N_3O environment. A packing diagram shows the existence of a centrosymmetric dimer in which two copper centers are intermolecularly linked by the O2 atom of the amide function, leading to a Cu_2O_2 unit.

1. Introduction

The oxidation of alkyl and aromatic substrates is an important quest for synthetic chemists. With this aspect in mind, the role of copper containing enzymes and their model complexes have been reviewed [1]. Reports pertaining to the oxidation of a $-CH_2-$ group linked to a 2-pyridyl and an amide or imine function by a suitable metal ion are rare [2,3]. A methylene group flanked by 2-pyridyl and an amine has been deprotonated on coordination to a Rh(-I, I) dimer and an Ir(I) center [4,5]. Very recently we have demonstrated the unprecedented formation of bis(carbonyl)amides from 2-aminomethyl substituted pyridine and quinoline, using copper(II) acetate [6]. This has prompted us to scrutinize the general applicability of this novel method to other substrates and herein we report the ready conversion of *ortho* aminomethyl substituted isoquinolines to their bis(isoquinolylcarbonyl)amides.

2. Experimental

2.1. Instrumentation and materials

A Perkin–Elmer Spectrum One FT-IR spectrometer (4000–250 cm^{-1}), Perkin–Elmer Lambda 25 UV–Vis spectrometer, Varian Mercury plus 400 MHz NMR spectrometer, Perkin–Elmer Series II CHNS/O Analyzer 2400, JEOL JES FA-200 X-band EPR spectrometer, waters Q-TOF premier mass spectrometer and a Lakshore VSM Setup for room temperature magnetic data, were used for performing the relevant measurements.

X-ray crystallographic data were collected using a Bruker SMART APEX-CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). The intensity data were corrected for Lorentz and polarization effects and empirical absorption corrections were applied using the SAINT program [7,8]. The structure of **1**·$2.5H_2O$ was solved by direct methods using SHELXS-97 [9]. Non-hydrogen atoms located from the difference Fourier maps were refined anisotropically by full-matrix least-squares on F^2, using SHELXL-97 [9]. All hydrogen atoms were included in calculated positions (except for the water of crystallization for which the hydrogen atoms could neither be added at calculated positions nor located from FMAP) and were refined isotropically using a riding model. The thermal displacement parameters of O9 and O10 are smeared and could not be improved with least squares refinement procedures.

2.2. General Procedures

Isoquinoline, 3-cyanoisoquinoline, *m*-chloroperbenzoic acid (MCPBA), dimethylcarbamyl chloride, (Aldrich, USA), trimethylsilylcyanide (Spectrochem), $Cu(OAc)_2{\cdot}H_2O$ (Merck India Ltd.) were used as received without further purification. Dichloromethane and chloroform were dried by standard methods.

2.3. Syntheses

2.3.1. Isoquinoline-N-oxide

IR (KBr, cm^{-1}): 1645(s), 1603(s), 1573(s), 1499(s), 1456(s), 1424(m), 1383(m), 1332(s), 1302(s), 1275(s), 1255(s), 1206(s),

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1171(vs), 1127(s), 981(w), 912(m), 868(m), 820(s), 748(s), 736(s), 629(m), 534(m), 494(m), 471(m). 400 MHz ^{1}H NMR (δ (J, Hz), $CDCl_3$): 7.614–7.633 (2H, m), 7.696 (1H, d, 6.8), 7.755 (1H, d, 7.2), 7.812 (1H, d, 8.8), 8.167 (1H, d, 8.4), 8.812 (1H, s).

2.3.2. Isoquinoline-1-carbonitrile

IR (KBr, cm^{-1}): 2228(s), 1637(s), 1622(s), 1580(m), 1552(m), 1492(m), 1455(m), 1389(s), 1344(m), 1322(w), 1297(w), 1226(w), 1198(w), 1032(m), 877(s), 838(s), 788(m), 746(s), 695(w), 660(m), 539(m), 464(m). 400 MHz ^{1}H NMR (δ (J, Hz), $CDCl_3$): 7.718 (2H, t, 7.6), 7.855 (1H, d, 5.2), 7.911 (1H, d, 8.0), 8.168 (1H, d, 8.4), 8.333 (1H, d, 8.4).

2.3.3. 1-Aminomethylisoquinoline (*1-ami*)

1-ami was isolated as a red solid. Yield: 1.9 g, 92%. IR (KBr, cm^{-1}): 3425(b), 1681(s), 1622(s), 1584(s), 1558(s), 1502(s), 1446(s), 1378(s), 1314(s), 1258(m), 1188(m), 1142(s), 1107(s), 1008(m), 956(m), 870(m), 827(s), 800(m), 746(s), 665(w), 634(w), 617(w), 593(w), 528(w), 503(w), 464(m), 439(w). 400 MHz ^{1}H NMR (δ (J, Hz), $CDCl_3$): 2.351 (NH_2, s), 4.543 (CH_2, s), 7.577 (1H, d, 5.2), 7.626 (1H, t, 7.8), 7.705 (1H, t, 7.4), 7.852 (1H, d, 8.4), 8.108 (1H, d, 8.8), 8.468 (1H, d, 5.6).

2.3.4. 3-Aminomethylisoquinoline (*3-ami*)

3-ami was isolated as a red solid. Yield: 0.925 g, 90%. IR (KBr, cm^{-1}): 3282(b), 1630(s), 1593(s), 1584(s), 1558(s), 1502(s), 1493(s), 1439(s), 1387(s), 1345(s), 1327(s), 1262(s), 1196(w), 1124(m), 1091(s), 1064(s), 1028(s), 957(s), 870(m), 881(s), 801(s), 751(s), 628(w), 488(w), 470(m). 400 MHz ^{1}H NMR (δ (J, Hz), $CDCl_3$): 2.772 (NH_2, s), 4.013 (CH_2, s), 7.440–7.601 (3H, m), 7.673 (1H, d, 8.0), 7.830 (1H, d, 8.4), 9.092 (1H, d, 11.2).

2.3.5. [Cu(*1-L*)(OAc)] (*1*)

To $Cu(OAc)_2{\cdot}H_2O$ (0.250 g, 1.25 mmol) dissolved in ethanol (80 mL) was added **1-ami** (0.396 g, 2.50 mmol) and the resulting mixture was stirred for 24 h with occasional purging of air. The solution was left undisturbed and a green precipitate deposited after two week of standing, which was collected and washed with ice-cold ethanol. Yield 0.380 g, 65%. IR (KBr, cm^{-1}): 1706(s), 1618(s), 1586(s), 1555(s), 1500(m), 1450(m), 1408(s), 1359(m), 1312(s), 1228(w), 1163(m), 1101(w), 1048(w), 1020(m), 929(w), 881(m), 834(m), 817(m), 763(m), 746(m), 710(w), 672(w), 636(m), 591(w), 518(w), 473(m), 288(w). UV–Vis [λ_{max}, nm (ε, M^{-1} cm^{-1}), DMF solution]: 710 (147), 373 (16975), 326 (29020). EPR (CH_3OH solution, 77 K): $g_{||} = 2.169$, $A_{||} = 85$ G; $g_{\perp} = 2.029$. μ_{eff} (polycrystalline, 25 °C) = 2.30 B.M. *Anal.* Calc. for $C_{22}H_{15}N_3O_4Cu$: C, 58.86; H, 3.37; N, 9.36. Found: C, 58.80; H, 3.32; N, 9.27%. ESI-MS: *m/z* Calc. for [^{63}Cu(**1-L**)]$^+$ 389.0226. Found 389.0224. Violet crystals of the composition **1**·2.5H_2O were obtained by slow evaporation of a methanol solution of **1**.

2.3.6. [Cu(*3-L*)(OAc)] (*2*)

To $Cu(OAc)_2{\cdot}H_2O$ (0.250 g, 1.25 mmol) dissolved in ethanol (50 mL) was added **3-ami** (0.396 g, 2.50 mmol) and the resulting mixture was stirred for 24 h with occasional purging of air. The solution was left undisturbed and a green precipitate of **2** deposited after a week, which was collected, washed with ice-cold ethanol and dried in *vacuo* over P_2O_5. Yield: 0.360 g, 65%. IR (KBr, cm^{-1}): 1701(s), 1613(s), 1578(s), 1494(w), 1460(s), 1390(m), 1332(s), 1313(s), 1254(m), 1149(w), 1111(w), 1052(w), 1018(w), 980(m), 912(m), 802(m), 786(w), 775(w), 747(m), 688(m), 651(w), 621(w), 588(w), 541(m), 498(w), 469(m), 371(w). UV–Vis [λ_{max}, nm (ε, M^{-1} cm^{-1}), MeOH solution]: 700 (126), 400 (7455), 365 (16280), 336 (22400). EPR (DMF solution, 77 K): $g_{||} = 2.164$, $A_{||} = 80$ G; $g_{\perp} = 2.016$. μ_{eff} (polycrystalline, 25 °C) = 2.31 B.M. *Anal.* Calc. for $C_{22}H_{15}N_3O_4Cu$: C, 58.86; H, 3.37; N, 9.36. Found: C, 58.78; H, 3.34; N, 9.30%. ESI-MS: *m/z* Calc. for [^{63}Cu(**3-L**)]$^+$ 389.0226. Found 389.0223.

2.3.7. Bis(1-isoquinolylcarbonyl)amide (*1-LH*)

Complex **1** (1.0 g, 2.02 mmol) and Na_2EDTA (1.50 g, 4.04 mmol) were dissolved in H_2O (50 mL) and stirred vigorously with 50 mL of $CHCl_3$ for 2 h. The $CHCl_3$ layer was separated, the aqueous layer was washed with $CHCl_3$ (2 × 30 mL) and the combined $CHCl_3$ solution was dried with anhydrous Na_2SO_4. After removal of the solvent, **1-LH** was obtained as a yellow solid. Yield: 0.60 g, 91%. IR (KBr, cm^{-1}): 1745(s), 1636(s), 1583(m), 1556(m), 1446(s), 1419(m), 1379(m), 1340(w), 1307(m), 1260(w), 1230(w), 1145(w), 1106(w), 1082(w), 1040(w), 1021(w), 913(w), 877(m), 831(m), 799(m), 746(m), 710(w), 640(w), 621(m), 511(w), 466(w). ESI-MS: *m/z* Calc. for $C_{20}H_{13}N_3O_2$ 327.1041, found (M$^+$–H) 328.1042. 400 MHz ^{1}H NMR (δ (J, Hz), $CDCl_3$): 7.754–7.779 (2H, m), 7.887–7.937 (2H, m), 8.671 (1H, d, 5.6), 9.638–9.663 (1H, m), 13.537 (NH, s). *Anal.* Calc. for $C_{20}H_{13}N_3O_2$ (327.34): C 73.38, H 4.00, N 12.84. Found: C 73.31, H 3.98, N 12.80%.

3. Results and discussion

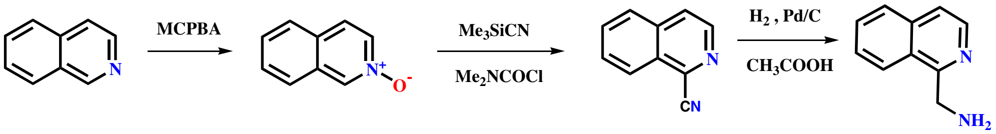
3.1. Synthesis

The following synthetic methodology [10] was adopted for the synthesis of 1-aminomethylisoquinoline (Scheme 1) and whilst the synthetic procedures are not detailed here, the spectroscopic data are included in the experimental section. In the first step, isoquinoline was converted to isoquinoline-*N*-oxide using *meta*-chloroperbenzoic acid in chloroform. A cyano group was introduced at the 1-position of the isoquinoline nucleus, using trimethylsilylcyanide in the presence of dimethylcarbamylchloride. This method offered 1-cyanoisoquinoline from isoquinoline-*N*-oxide in good yields. 1-Cyanoisoquinoline was then converted to **1-ami** by reduction with molecular hydrogen in the presence of a Pd/C catalyst in acetic acid. Commercially available 3-cyanoisoquinoline was converted to **3-ami** in a similar manner.

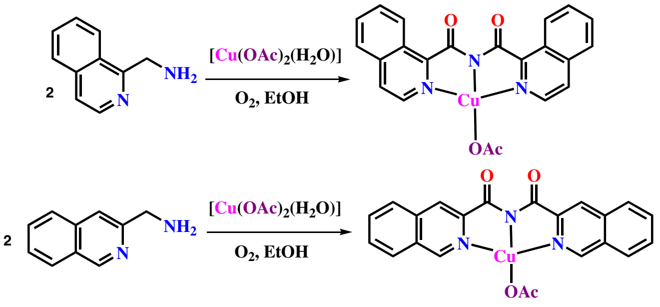
An ethanolic solution of **1-ami**, on stirring with half equivalent of [$Cu(OAc)_2(H_2O)$] in air, generated a green solution which on standing deposited a green precipitate of the composition [Cu(**1-L**)(OAc)] (**1**) in a good yield, as shown in Scheme 2. In a similar manner, **3-ami** also reacted with copper(II) acetate affording [Cu(**3-L**)(OAc)] (**2**) in similar yields {**1-L** = bis(1-isoquinolylcarbonyl)amide ion and **3-L** = bis(3-isoquinolylcarbonyl)amide ion}. The reported compounds **1** and **2** were not obtained if the reaction was carried out under anaerobic conditions. It is pertinent to note that other mononuclear copper(II) salts did not show the observed conversion [11–13] and a related 2-(aminomethyl)pyridine on reaction with copper(II) acetate in acetonitrile yielded a simple coordination product [13]. It has also been previously observed that bis(2-picolyl)amine yields a simple coordinated complex and does not show oxidation of the methylene group under the same [6] and other conditions [14]. Free **1-LH** was isolated as a yellow crystalline solid from **1** by extrusion of the Cu^{2+} ion using Na_2EDTA.

3.2. Molecular structure

The molecular structure of **1**·2.5H_2O has been established using the single crystal X-ray diffraction method. The complex crystallized in the $P\bar{1}$ space group (Table 1) and the asymmetric unit contained **1** and lattice water molecules. The copper(II) center has a pseudo square-planar N_3O environment (Fig. 1) and has a distorted geometry. The two chelate bite angles have a value of 81.5(1)° and 81.9(1)°, while the two non-chelated *cis* angles are 97.9(1)° and 98.7(1)°. The two *trans* angles are N1–Cu1–N3, 163.4(1) and N2–Cu1–O3,



Scheme 1. Synthesis of **1-ami**.



Scheme 2. Synthesis of **1** and **2**.

179.2(1)°. The Cu–N$_Q$ (N$_Q$ = isoquinolyl-N and N$_A$ = amide-N) distances are longer by 0.085(3) and 0.066(3) Å than the Cu–N$_A$ and Cu–O distances, respectively. The bond parameters around the coordination environment are listed in Table 2.

In the packing diagram the complex exists as a centrosymmetric dimer in which two copper centers are intermolecularly linked by the O2 atom of the amide function (Fig. 2). As a result a Cu$_2$O$_2$ unit is present with the Cu1–O2 contact having a length of 2.753(3) Å. In this unit, the non-bonded Cu···Cu, O2···O2 and O2···Cu distances, respectively, are 5.1218(5), 4.528(3) and 3.973(2) Å. The angles subtended at Cu1 and O2, respectively, are 82.5(1)° and 97.5(1)°. As a result of O2 linking, the C11 and O2 atoms of the amide function deviate respectively by 0.18 and 0.64 Å from the plane containing the O1C10N2C12 atoms.

Also a π···π interaction between the isoquinolyl rings is present, with a distance of 3.57 Å between the centroids formed by the N1C1C2C3C8C9 and C13C14C15C16C1718 atoms. The aromatic rings of the complex form hydrophobic layers and water molecules

Table 1
Crystallographic data for **1**·2.5H$_2$O.

Formula	$C_{44}H_{40}N_6O_{13}Cu_2$
Formula weight	987.91
T (K)	293(2)
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.5812(7)
b (Å)	11.0568(7)
c (Å)	11.3189(8)
α (°)	80.081(4)
β (°)	66.806(4)
γ (°)	78.244(4)
V (Å^3)	1185.44(14)
Z	1
D_{calc} (g cm^{-3})	1.482
μ (mm^{-1})	0.977
Goodness-of-fit (GOF)[a] on F^2	1.054
$R[I > 2\sigma(I)]$	[b]R_1 = 0.0532; [c]wR_2 = 0.1560
$R_{indices}$ (all data)	[b]R_1 = 0.0690; [c]wR_2 = 0.1689

[a] $\mathrm{GOF} = [\sum[w(F_0^2 - F_c^2)^2]/M - N]^{1/2}$ (M = number of reflections, N = number of parameters refined).

[b] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$.

[c] $wR_2 = [\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]]^{1/2}$.

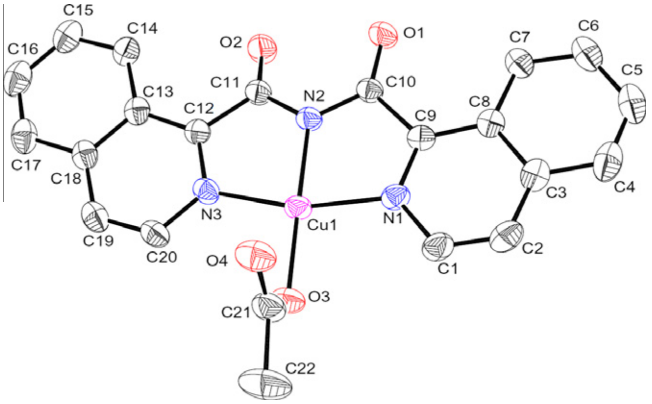


Fig. 1. ORTEP (30% probability) diagram of **1**, H-atoms are omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) in **1**·2.5H$_2$O.

Cu1–N1	1.992(3)	N1–Cu1–N2	81.5(1)
Cu1–N2	1.909(2)	N1–Cu1–N3	163.4(1)
Cu1–N3	1.995(3)	N1–Cu1–O3	97.9(1)
Cu1–O3	1.928(2)	N1–Cu1–O4	96.7(1)
Cu1–O4	2.736(3)	N1–Cu1–O2A	92.9(1)
Cu1–O2A	2.753(3)	N2–Cu1–N3	81.9(1)
		N2–Cu1–O3	179.1(1)
		N2–Cu1–O4	128.2(1)
		N2–Cu1–O2A	91.32(9)
		N3–Cu1–O3	98.7(1)
		N3–Cu1–O4	93.3(1)
		N3–Cu1–O2A	87.7(1)
		O3–Cu1–O4	52.5(1)
		O3–Cu1–O2A	88.1(1)
		O2A–Cu1–O4	140.3(1)

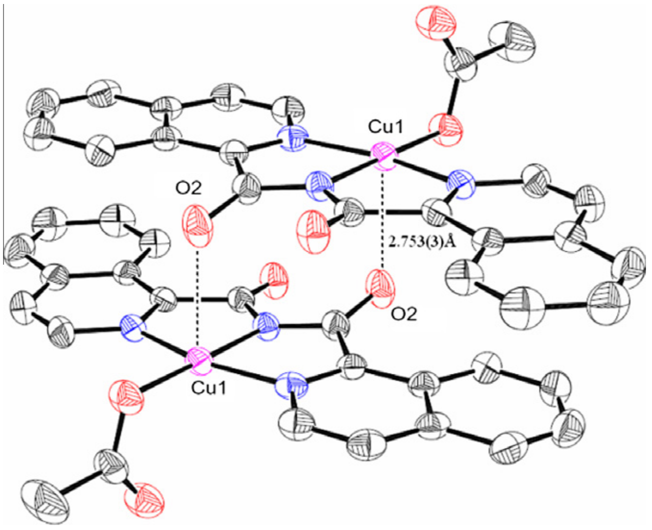


Fig. 2. ORTEP (30% probability) diagram depicting the dimer containing Cu$_2$O$_2$ unit found in **1**·2.5H$_2$O, H-atoms are omitted for clarity.

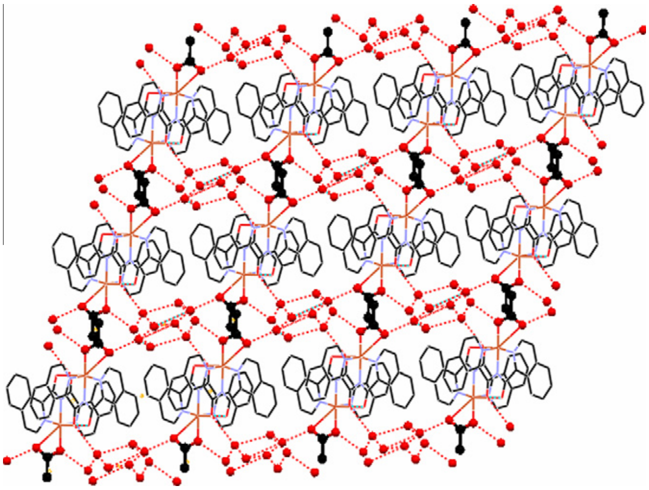


Fig. 3. Packing diagram of **1**·2.5H_2O, viewed down the *b*-axis.

Table 3
Selected non-bonded distances (Å) and angles (°) in **1**·2.5H_2O.

D···A	Distance	Symmetry operator
O1···O2	2.815(5)	–
O1···O6	2.876(5)	–
O3···O5	2.825(5)	–
O5···O6	2.908(8)	$-x+1, -y+1, -z+1$
O5···O7	2.79(1)	$-x+1, -y+1, -z+1$
O6···O7	2.79(1)	$-x+1, -y+1, -z+1$
	Angle	
O6···O5···O7	139.6(3)	
O5···O6···O7	106.2(3)	
O6···O7···O5	110.2(3)	

are amalgamated between these layers. The water molecules are further confined into a channel in which the methyl group of the acetate ion serves as a separator of the layers containing water molecules (Fig. 3). The water molecules form a cyclic centrosymmetric hexamer (O5, O6 and O7), having a chair shape [15], and are linked to O9 and O10. Relevant non-bonded distances and angles are included in Table 3. These are also linked to the complex molecule through hydrogen bonds with the carbonyl oxygen atom O1 through O6···O1, 2.88(1) Å as well as to the acetate oxygen atom O4, through O4···O5, 2.83(1) Å and O4···O9, 2.77(1) Å non-bonded interactions.

3.3. Spectra

The IR spectrum of **1** shows a characteristic 1706 cm^{-1} peak for ν_{CO}, which shifts to 1745 cm^{-1} in the free **1-LH**, and **2** shows the same peak at 1701 cm^{-1}. The ESI-MS of **1** exhibits $m/z = 389.0224$ (Calc. 389.0226) that can be assigned to the $[^{63}Cu(\mathbf{1\text{-}L})]^+$ fragment. In the case of **2**, a peak at $m/z = 389.0223$ corresponding to the $[^{63}Cu(\mathbf{3\text{-}L})]^+$ fragment was observed. Free **1-LH** shows a $m/z = 328.1042$ peak in the ESI-MS for the $\mathbf{1\text{-}LH_2}^+$ fragment. The room temperature magnetic moments of **1** and **2** are ~2.30 B.M., being assigned as one electron paramagnets. The EPR spectra of both complexes in frozen solution (77 K) exhibit a typical axial spectrum with $g_{||} > g_{\perp} > 2$, consistent with a $b_1{}^1$ ground electronic configuration for the Cu^{2+} ion.

4. Conclusion

In conclusion, *ortho* aminomethyl substituted isoquinolines readily form the respective bis(carbonyl)amide complexes on treatment with $[Cu(OAc)_2(H_2O)]$ in air and in hydrated ethanol. This reaction involves oxidation of the methylene group and formation of a bond between nitrogen and carbon in N–C(=O) through coupling. The determination of the molecular structure of **1**·2.5H_2O confirmed the presence of a bis(1-isoquinolylcarbonyl)amide complex of the copper(II) ion. Other spectroscopic evidence corroborates the observed conversion. With this result we believe that an *ortho* aminomethyl substituted pyridine nucleus having alkyl/aryl substituents or having fused aromatic/carbocyclic rings can be converted to the respective bis(carbonyl)amides, using copper(II) acetate in ethanol and in the presence of molecular oxygen. Our investigations in this direction are under scrutiny.

Acknowledgments

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Appendix A. Supplementary data

CCDC 809572 contains the supplementary crystallographic data for compound **1**·2.5H_2O. 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.10.038.

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