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Conversion of 2-(aminomethyl) substituted pyridine and quinoline to their dicarbonyldiimides using copper(II) acetate

Rojalin Sahu, Sumanta Kumar Padhi, Himanshu Sekhar Jena, Vadivelu Manivannan *

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India

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ABSTRACT

In air, hydrated ethanolic (95%) solution of 2-(aminomethyl) substituted pyridine and quinoline, on stirring with half equivalent of $Cu(OAc)_2 \cdot H_2O$, respectively afforded [Cu(**bpca**)(OAc)(H_2O)]·H_2O (**1**) and [Cu(**bqca**)(OAc)(H_2O)] (**2**) {**bpca** = bis(2-pyridylcarbonyl)diimide ion and **bqca** = bis(2-quinolylcarbonyl)diimide ion} in good yields. These reactions involve oxidation of the methylene group and formation of the bond between nitrogen and carbon in N–C(=O) through coupling. The complex [Cu(**pqca**)(OAc)(H_2O)]$_3$[$Cu_2(OAc)_4(EtOH)_2$]$_{1.5}$ (**3**) {**pqca** = (2-pyridylcarbonyl)(2-quinolylcarbonyl)diimide ion} was synthesized by stirring an ethanolic solution of the Schiff base [(2-pyridyl)-N-((2-quinolyl)methylene)methanamine] (**L1**) and with one equivalent of $Cu(OAc)_2 \cdot H_2O$. A plausible mechanism for the conversion has been proposed. The free ligands were isolated as crystalline solids from compounds **1**–**3**, by extrusion of Cu^{2+} ion using $EDTA^{2-}$. The molecular structures of **1**–**3** and **bqcaH** were established by X-ray crystallography and compounds having quinolyl group have π-stacking interactions.

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1. Introduction

Oxidation of alkyl and aromatic substrates by copper containing enzymes and by the model complexes using dioxygen is an active area of research [1]. However, oxidation of the $-CH_2-$ group flanked by a 2-pyridyl and an amide/imine function in the presence of a suitable metal ion is rare [2,3]. In such cases the final ligand that was found using the amide/imine function as 2-pyridylcarbonylamide/2-pyridylaldimine is bis(2-pyridylcarbonyl)amide ion (**bpca**) and as 2-pyridylmethylketimine is 4′-(2-pyridyl)-2,2′:6′,2″-terpyridine. The chemical reactivity of the methylene group flanked by a 2-pyridyl and an amine function is: (a) deprotonation of the coordinated bis(picolyl)amine (**bpa**) using a strong base, firstly at the secondary nitrogen atom, [{Rh(nbd)}$_2$(μ-**bpa**–H)]Cl and then at the methylene group to PyCH=N–CH$_2$Py in [{Rh(nbd)}$_2$(μ-**bpa**–2H)] followed by its oxidation to [PyC(O)–N–CH$_2$Py]$^-$ (bpam–H) in [Rh(nbd)(bpam–H)] using O_2 [4] and (b) double deprotonation of the coordinated bis(picolyl)amine using KO^{t}Bu as in K[Ir(**bpa**–2H)(cod)] followed by chemical oxidation to a ligand radical complex [Ir(**bpa**–2H)(cod)] using Ag^+ or O_2 [5], as shown in Scheme 1.

The **bpca**$^-$ ligand was obtained through the Cu(II) ion mediated hydrolysis of 2,4,6-tris(2-pyridyl)-1,3,5-triazine [6,7] and has been used for the synthesis of complexes of several transition metal ions. In metal chelates the three nitrogen atoms are coordinated to the metal center leaving two oxygen atoms available for further coordination. Thus the metal chelates of **bpca**$^-$ ion can act as a bidentate ligand and such coordination by the oxygen atoms has been exploited to build supramolecular assemblies having extended structures [8–18].

This work stems from our interest in using picolylamines as synthon for synthesis of nitrogenous ligands [19] and herein we describe the method in which 2-(aminomethyl) attached to a pyridine or quinoline ring can be readily converted to respective dicarbonyldiimides, using copper(II) acetate. The compounds obtained, by using 2-(aminomethyl)pyridine (**2-amp**) is [Cu(**bpca**)(OAc)(H_2O)]·H_2O and by using 2-(aminomethyl)quinoline (**2-amq**) is [Cu(**bqca**)(OAc)(H_2O)] {bqca = bis(2-quinolylcarbonyl)diimide ion}. In addition, the synthesis of [Cu(**pqca**)(OAc)(H_2O)]$_3$[$Cu_2(OAc)_4$-(EtOH)$_2$]$_{1.5}$ {**pqca** = (2-pyridylcarbonyl)(2-quinolylcarbonyl)diimide ion} from a Schiff base [(2-pyridyl)-N-((2-quinolyl)methylene)methanamine] and copper(II) acetate are described. The structural evaluation of these compounds and that of the ligand **bqcaH** are discussed.

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,

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* Corresponding author. Tel.: +91 361 258 2306; fax: +91 361 258 2349.
E-mail address: mani@iitg.ernet.in (V. Manivannan).

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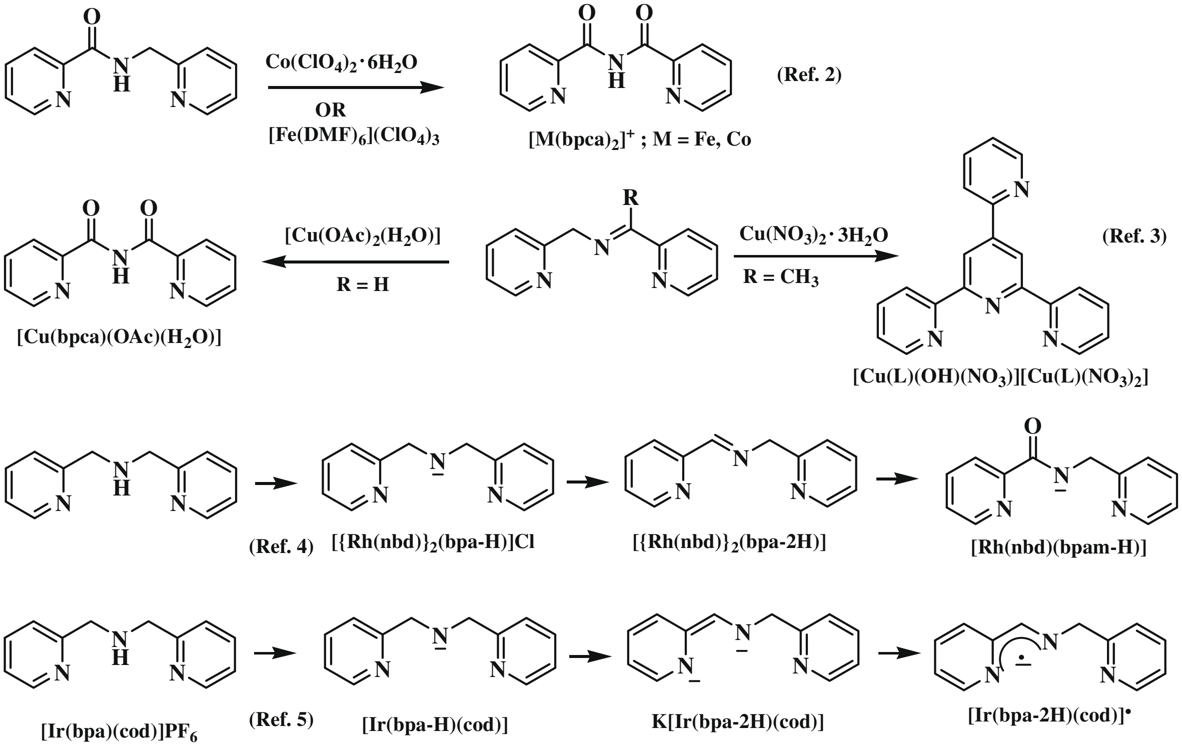


Scheme 1.

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 Bruker SMART APEX-CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). The intensity data were corrected for Lorentz and polarization effects and empirical absorption corrections was applied using SAINT program [20]. All the structures were solved by direct methods using SHELXS-97 [21,22]. Non-hydrogen atoms located from the difference Fourier maps were refined anisotropically by full-matrix least-squares on F^2 using SHELXL-97 [21,22]. All hydrogen atoms included at the calculated positions (except for the water/ethanol molecules, in which some of the hydrogen atoms could neither be added at calculated positions nor be located from FMAP) were refined isotropically using a riding model. Hence in **3**, some of the C–H bonds will not be ideal and may vary. In **bqcaH**, all the hydrogen atoms were located from the FMAP and were refined anisotropically.

2.2. General procedures

2-(Aminomethyl)pyridine, 2-quinolinecarboxaldehyde (Aldrich, USA), $Cu(OAc)_2{\cdot}H_2O$ (Merck India Ltd), ethanol (Bengal Chemicals & Pharmaceuticals Ltd., Kolkata), and other reagent grade chemicals were used as received without further purification. Bis(picolyl)amine was prepared by following the reported procedures [23].

2.3. Syntheses

2.3.1. 2-Quinolinecarbaldoxime

To a solution of 2-quinolinecarboxaldehyde (1 g, 6.3 mmol) and hydroxylamine hydrochloride (1 g, 14.4 mmol) in ethanol (10 mL), pyridine (1 mL) was added and refluxed for 6 h. After removing the solvent, ice-cold water (10 mL) was added, and a yellow precipitate of the 2-quinolinecarboxaldoxime was isolated by filtration, washed with ice-cold water and dried in desiccators [24]. The crude product was used directly in the next step without further purification. Yield: 0.9 g, 83%. IR (KBr, cm^{-1}): 3415 (m), 1635(s), 1603(m), 1563(m), 1504(m), 1489(w), 1455(m), 1427(m), 1354(m), 1321(w), 1302(w), 1238(w), 1206(w), 1141(w), 1118(w), 1022(s), 1007(s), 944(m), 922(m), 903(m), 839(m), 828(s), 792(m), 776(w), 741(s), 680(m), 633(m), 588(m), 476(m). 400 MHz ^1H NMR (δ (*J*, Hz), $CDCl_3$): 7.57(1H, t, 7.4), 7.74 (1H, t, 7.6), 7.73 (1H, d, 8.0), 7.94 (1H, d, 8.4), 8.11 (1H, d, 8.8), 8.16 (1H, d, 8.4), 8.41 (1H, s), 8.63 (OH, b).

2.3.2. 2-(Aminomethyl)quinoline

In a 200 mL round-bottomed flask equipped with overhead mechanical stirring, the 2-quinolinecarboxaldoxime (3.5 g, 20 mmol) and acetic acid (32 mL) were dissolved in ethanol (50 mL). Zinc dust (32 g) was added in small increments over 1 h and the mixture was stirred at room temperature for another 12 h. The mixture was filtered, washed with ethanol and the combined filtrate and washings were concentrated in *vacuo*. The concentrate was made strongly basic (pH >12) using saturated aqueous KOH solution and extracted with ether. The ether solution was dried over anhydrous Na_2SO_4 and **2-amq** was recovered as oil after removal of ether [24]. Yield: 2.4 g, 73%. IR (KBr, cm^{-1}): 3400(m), 2962(s), 2926(s), 1606(s), 1583(m), 1484(s), 1418(m), 1376(m), 1309(m), 1290(m), 1261(m), 1176(w), 1155(w), 1109(m), 1086(w), 1034(w), 905(w), 746(s), 481(w). 400 MHz ^1H NMR (δ (*J*, Hz), $CDCl_3$): 1.98 (NH_2, s), 4.14 (CH_2, s), 7.37 (1H, d, 8.4), 7.49 (1H, t, 7.2), 7.68 (1H, t, 6.8), 7.78 (1H, d, 8.0), 8.04 (1H, d, 8.4), 8.09 (1H, d, 8.8).

2.3.3. [Cu(**bpca**)(OAc)(H2O)]·H2O (**1**)

To $Cu(OAc)_2{\cdot}H_2O$ (1.1 g, 5.5 mmol) dissolved in ethanol (60 mL) was added **2-amp** (1.2 g, 11 mmol) and stirred for 24 h. The solution was left undisturbed, blue crystals of **1** deposited after a week were collected and washed with ice-cold ethanol.

Yield: 1.3 g, 61%. Selected IR frequencies (KBr, cm^{-1}): 1717(s), 1635(s), 1566(m), 1413(m), 1383(s), 1361(s). *Anal.* Calc. for $C_{14}H_{15}N_3O_6Cu$ (384.8): C, 43.69; H, 3.93; N, 10.92. Found: C, 43.61; H, 3.91; N, 10.75%.

2.3.4. [Cu(**bqca**)(OAc)(H_2O)] (**2**)

Compound **2** was prepared by following the same procedure described for **1**, and using 3 mmol of **2-amq** (0.506 g) and 1.5 mmol of $Cu(OAc)_2{\cdot}H_2O$ (0.300 g). Yield: 0.400 g, 58%. IR (KBr, cm^{-1}): 1707(s), 1633(s), 1512(w), 1462(m), 1379(s), 1345(w), 1270(w), 1218(w), 1151(w), 1118(w), 1026(w), 854(m), 779(s), 615(w). UV–Vis [λ_{max}, nm(ε, $M^{-1}\,cm^{-1}$), CH_3OH solution]: 730 (65); 510 (70); 240 (38595). EPR (CH_3OH solution, 77 K): $g_{||} = 2.263$, $A_{||} = 82$ G; $g_{\perp} = 2.082$. μ_{eff} (polycrystalline, 25 °C) = 2.20 B. M. *Anal.* Calc. for $C_{22}H_{16}N_3O_5Cu$ (466): C, 56.71; H, 3.46; N, 9.02. Found: C, 56.62; H, 3.43; N, 9.11%.

2.3.5. [Cu(**pqca**)(OAc)(H_2O)]$_3$[$Cu_2(OAc)_4(EtOH)_2$]$_{1.5}$ (**3**)

A mixture of **2-amp** (0.11 g, 1 mmol) and 2-quinolinecaboxaldehyde (0.16 g, 1 mmol) in methanol (30 mL) were heated at reflux for 5 h and then evaporated to dryness, which afforded [(2-pyridyl)-N-((2-quinolyl)methylene)methanamine] (**L1**) as a reddish brown oil. IR (KBr, cm^{-1}):1633(s), 1595 (m), 1503 (m), 1471 (w), 1458 (w), 1434 (m), 1384 (m), 1307 (w), 1148 (w), 1116(w), 1093 (w), 1054 (w), 999 (w), 913 (w), 830 (m), 750 (s), 624 (m), 477 (w). 400 MHz ^{1}H NMR (δ (*J*, Hz), $CDCl_3$): 5.09 (CH_2, s), 7.19 (1H, t, 5.8), 7.45 (1H, d, 7.6), 7.57 (1H, t, 7.4), 7.68 (1H, t, 7.6), 7.74 (1H, t, 7.6), 7.83 (1H, d, 8.0), 8.14 (1H, d, 8.4), 8.19 (1H, d, 8.0), 8.24 (1H, d, 8.4), 8.60 (1H, d, 4.4), 8.73 (1H, s). The crude **L1** was dissolved in ethanol (30 mL), an ethanolic solution (30 mL) of $Cu(OAc)_2{\cdot}H_2O$ (0.2 g, 1 mmol) was added and stirred for 48 h. The solution was left undisturbed and green crystals deposited after two weeks were collected after washing with ice-cold ethanol. Yield: 0.167 g, 52% (per copper atom). IR (KBr, cm^{-1}): 1706(s), 1632(s), 1461(m), 1376(s), 1342(m), 1217(w), 1117(w), 851(w), 803(m), 778(s), 725(m), 512(w). UV–Vis [λ_{max}, nm(ε, $M^{-1}\,cm^{-1}$), CH_3OH solution]: 680 (190), 450 (160), 321 (6885), 283 (11040), 243 (27820). EPR (CH_3OH solution, 77 K): $g_{||} = 2.237$, $A_{||} = 75$ G; $g_{\perp} = 2.041$. μ_{eff} (polycrystalline, 25 °C) = 1.97 B. M. (per Cu atom). *Anal.* Calc. for $C_{72}H_{81}N_9O_{30}Cu_6$ (1933.7): C, 44.72; H, 4.22; N, 6.52. Found: C, 44.60; H, 4.18; N, 6.45%.

2.3.6. [Cu(**bpa**)$(OAc)_2$]$\cdot 3H_2O$

To 0.2 g (1 mmol) of the **bpa** dissolved in 10 mL of 95% ethanol, an ethanolic (20 mL) solution of 0.2 g (1 mmol) of $Cu(OAc)_2{\cdot}H_2O$ was added. The solution was stirred for 6 h, which afforded a green gummy substance after few days of standing, which was dissolved in acetonitrile and left undisturbed. The blue crystals deposited were collected, which lost its crystallinity quickly, were finely ground and kept in vacuum desiccators over P_4O_{10}. Yield: 0.20 g, 46%. IR (KBr, cm^{-1}): 2962(m), 2923(m), 2853(m), 1586(s), 1567(s), 1409(s), 1261(s), 1093(s), 1025(s), 803(s). UV–Vis [λ_{max}, nm(ε, $M^{-1}\,cm^{-1}$), CH_3OH solution]: 637 (60); 450 (25), 256 (12470). *Anal.* Calc. for $C_{16}H_{25}N_3O_7Cu$ (434.9): C, 44.18; H, 5.79; N, 9.66. Found: C, 44.12; H, 5.70; N, 9.55%.

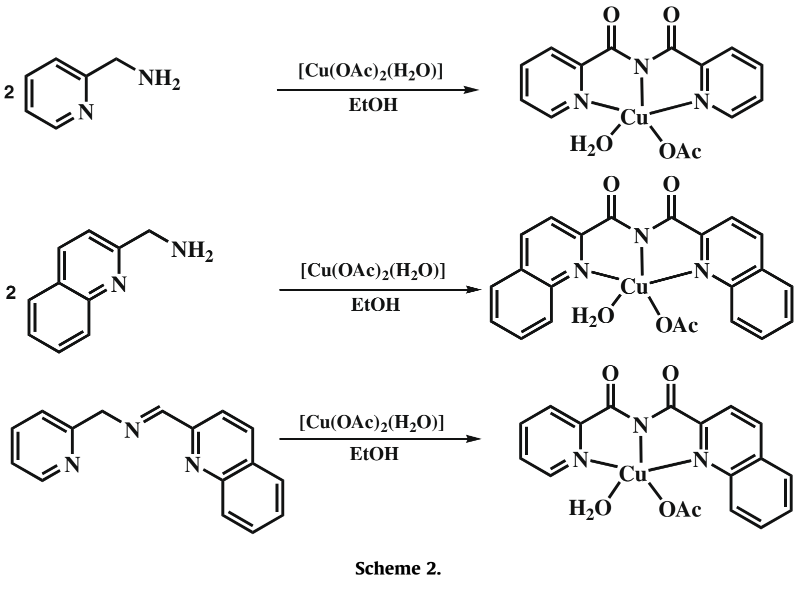
2.4. Free ligands

Free **bpcaH**, **bqcaH** and **pqcaH** {pqcaH = (2-pyridylcarbonyl)(2-quinolylcarbonyl)diimide} were obtained respectively from **1**, **2** and **3** by extrusion of Cu^{2+} ion using Na_2EDTA. In a typical procedure, the complex (0.1 mmol) and Na_2EDTA (100 mg, 0.27 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, dried with anhydrous Na_2SO_4, and the free ligands were obtained in quantitative yields after removing $CHCl_3$. **bqcaH**: m.p. 242 °C. ESI-MS: *m/z Anal.* calc. for $C_{20}H_{13}N_3O_2$ 327.10. Found (M^-–H) 325.94%. IR, (KBr, cm^{-1}): 1753 (s), 1708(m), 1588(w), 1478(w), 1463(s), 1434(s), 1384(m), 1275(m), 1180(w), 1117(m), 1095(m), 848(w), 778(w), 742(m), 722(m), 693(s), 663(w), 618(w), 541(m), 492(w). 400 MHz ^{1}H NMR (δ (*J*, Hz), $CDCl_3$): 7.70 (2H, t, 7.2), 7.88 (2H, t, 7.6), 7.94 (2H, d, 8.4), 8.40 (6H, m), 13.65 (NH, s). **pqcaH**: m.p. 182 °C. ESI-MS: *m/z Anal.* calc. for $C_{16}H_{11}N_3O_2$ 277.09. Found (M^-–H) 275.95%. IR, (KBr, cm^{-1}): 1753(s), 1588(w), 1469(s), 1424(s), 1261(s), 1205(m), 1100(s), 1024(w), 996(w), 871(w), 846(m), 798(w), 772(m), 746(m), 691(m), 663(m), 618(m), 591(w), 477(w). 400 MHz ^{1}H NMR (δ (*J*, Hz), $CDCl_3$): 7.57(1H, t, 6.2), 7.71(1H, t, 6.0), 7.88(3H, m), 8.31(1H, d, 8.0), 8.40(3H, m) 8.79(1H, d, 4.8), 13.27 (NH, s).

3. Results and discussion

3.1. Synthesis

In air, hydrated ethanolic (95%) solution of **2-amp** on stirring with half equivalent of $Cu(OAc)_2{\cdot}H_2O$ generated a green solution



Scheme 2.

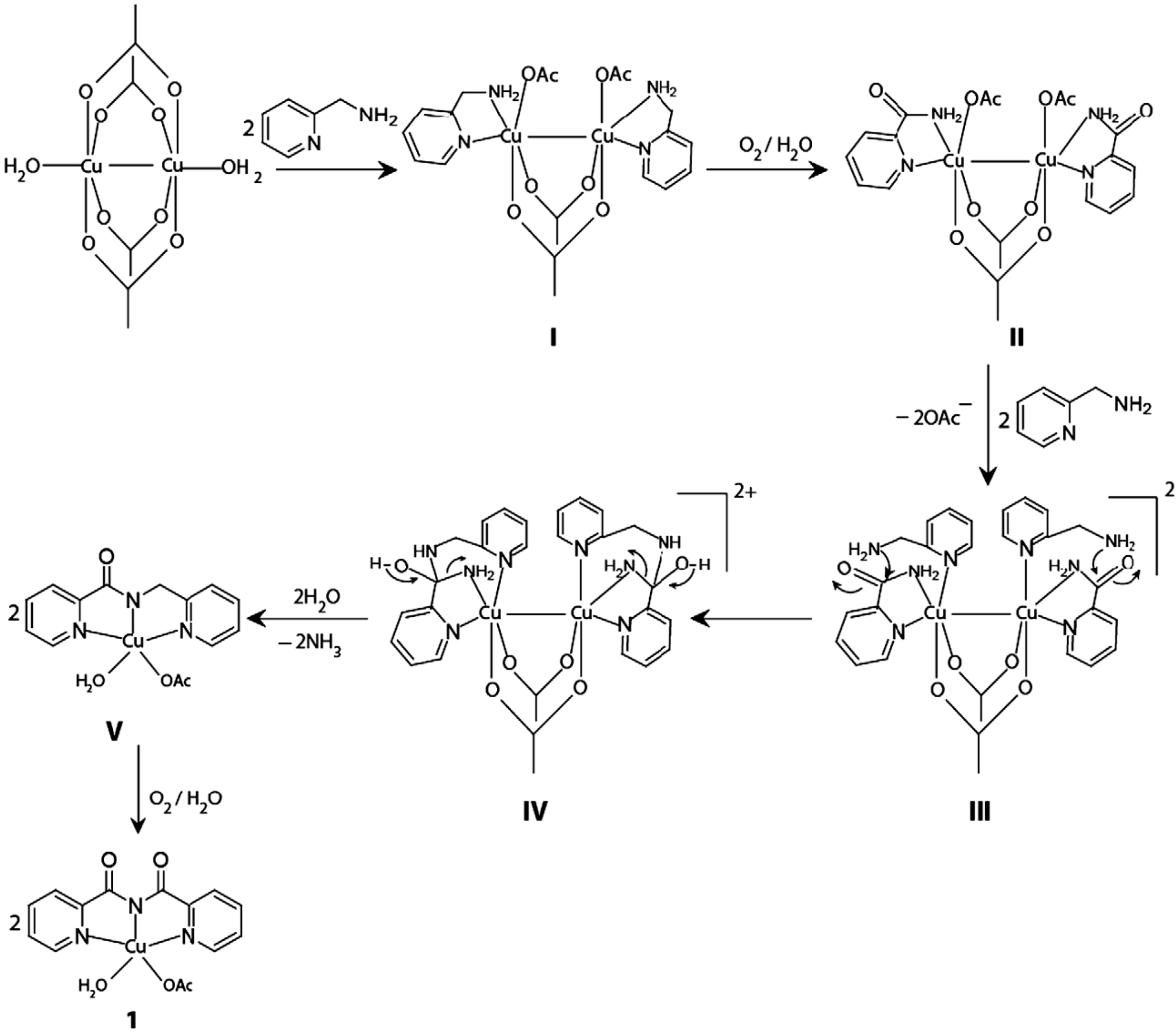
which on standing deposited blue crystals of composition [Cu(**bpca**)(OAc)(H_2O)]·H_2O (**1**) in good yields (Scheme 2). Under the same conditions by using **2-amq**, green crystals of [Cu(**bqca**)(OAc)(H_2O)] (**2**) were obtained. These reactions clearly involve two categories of reactivities under mild conditions: (1) the oxidation of the methylene function and (2) formation of the bond between nitrogen and carbon in N–C(=O) through coupling.

A plausible mechanism for the conversion is shown in Scheme 3. Coordination of one molecule of **2-amp** at each of the copper atoms in dicopper(II) center form **I**. Oxidation of the methylene group might occur at this stage leading to an amide intermediate **II**. Coordination of another molecule of **2-amp** through the pyridine nitrogen atom with a pendent 2-aminomethyl group will lead to **III**. Since the carbonyl carbon of the amide function is now nucleophilic in character due to loss of conjugation with the lone-pair on –NH_2 group (which is coordinated to copper), will be attacked by pendent 2-aminomethyl group, forming the intermediate **IV** containing tetrahedral carbon centers. Elimination of ammonia from tetrahedral carbon, collapse of the dicopper core to intermediate **V** that contain *N*-(2-picolyl)picolinamide moiety and its oxidation to bis(2-pyridylcarbonyl)diimide lead to the final product **1**.

Under the same experimental conditions, **bpa** and Cu(OAc)$_2$·H_2O yielded the compound of composition [Cu(**bpa**)(OAc)$_2$]·3H_2O, in which coordination of the tridentate ligand to the copper(II) center occurs and above noted reactivity was not observed. It is pertinent to note that the oxidation of the methylene group adjacent to a pyridine-2-carboxamido moiety in N-(2-picolyl)picolinamide by Fe(III), Co(III) ions and adjacent to a pyridine-2-methylketimine function in N-(2-pyridylmethyl)pyridine-2-methylketimine by Cu(NO$_3$)$_2$·3H_2O were reported earlier [2,3]. The complex [Cu(**pqca**)(OAc)(H_2O)]$_3$[Cu$_2$(OAc)$_4$(EtOH)$_2$]$_{1.5}$ (**3**) was synthesized by using the Schiff base [(2-pyridyl)-N-((2-quinolyl)methylene)methanamine] (**L1**) and one equivalent of Cu(OAc)$_2$·H_2O. In this reaction the imine moiety is oxidized to 2-quinoline-2-carboxamido moiety, which probably aids the oxidation of the adjacent methylene group. It is relevant to note that reaction of **2-amp** with Cu(OAc)$_2$·H_2O in acetonitrile produced a simple bischelate [25]. The free ligands were isolated as crystalline solids from the compounds **1–3**, by extrusion of Cu^{2+} ion using EDTA^{2-}.

3.2. Molecular structures

The molecular structures of **1–3** and of **bqcaH** were established by single crystal X-ray diffraction methods and the crystal data are listed in Table 1. The crystallographic and bond parameters of **1** prepared by this method, are identical to that reported for **1** prepared by other two routes viz., by reacting



Scheme 3. Plausible mechanism for the conversion of **2-amp** to **1**.

Table 1
Crystallographic and refinement parameters.

	1	2	3	4
Formula	$C_{14}H_{15}CuN_3O_6$	$C_{22}H_{16}N_3O_5Cu$	$C_{72}H_{81}N_9O_{30}Cu_6$	$C_{20}H_{13}N_3O_2$
CCDC number	284749	754807	754808	754809
Formula weight	384.84	465.93	1933.73	327.33
Crystal color, habit	blue, blocks	green, blocks	green, blocks	brown, blocks
T (K)	298(2)	298(2)	298(2)	298(2)
Crystal system	triclinic	orthorhombic	triclinic	monoclinic
Space group	$P\bar{1}$	Cmc2$_1$	$P\bar{1}$	$P2_1$/n
a (Å)	7.3954(2)	16.2378(13)	14.764(2)	9.1492(4)
b (Å)	8.6190(3)	15.5732(13)	16.575(3)	13.1027(6)
c (Å)	13.0051(4)	15.9288(14)	17.431(3)	13.4468(6)
α (°)	74.610(2)	90	72.615(12)	90
β (°)	84.771(2)	90	76.271(12)	96.080(3)
γ (°)	81.008(2)	90	80.499(11)	90
V (Å$^{3)}$	788.34(4)	4028.0(6)	3934.0(12)	1602.92(12)
Z	2	8	2	4
D_{calc} (g cm^{-3})	1.621	1.537	1.633	1.356
μ (mm^{-1})	1.422	1.125	1.683	0.090
F(0 0 0)	1.031	1856	1980	680
Goodness-of-fit (GOF)[a] on F^2	1.79	1.050	1.039	1.040
R [$I > 2\sigma(I)$]	[b]R_1 = 0.0179, [c]wR_2 = 0.0179	[b]R_1 = 0.1075, [c]wR_2 = 0.2147	[b]R_1 = 0.0789, [c]wR_2 = 0.1688	[b]R_1 = 0.0420, [c]wR_2 = 0.0978
R indices (all data)	[b]R_1 = 0.0514, [c]wR_2 = 0.0514	[b]R_1 = 0.1077, [c]wR_2 = 0.2147	[b]R_1 = 0.1297, [c]wR_2 = 0.1927	[b]R_1 = 0.0797, [c]wR_2 = 0.1128

[a] GOF = $[\sum[w(F_0{}^2-F_c{}^2)^2]/M-N]^{1/2}$ (M = number of reflections, N = number of parameters refined).
[b] $R_1 = \sum||F_0|-|Fc||/\sum|F_0|$.
[c] $wR_2 = [\sum[w(F_0{}^2-F_c{}^2)^2]/\sum[w(F_0{}^2)^2]]^{1/2}$.

$Cu(OAc)_2{\cdot}H_2O$ with 2,4,6-tris(2-pyridyl)-1,3,5-triazine [26] and with N-(2-pyridylmethyl)pyridine-2-carbaldimine [3], hence its structural details are not elaborated further. The selected bond distances and angles for **2, 3** and **bqcaH** are listed in Table 2.

Compound **2** crystallized in the space group $Cmc2_1$ and the asymmetric unit contain 2 half molecules. Compound **3** is a co-crystal that crystallized in the space group $P\bar{1}$ and the unit cell contain 3 units of the [Cu(**pqca**)(OAc)(H_2O)] (**3a**) and 1.5 units [$Cu_2(OAc)_4(EtOH)_2$] (**3b**). A perspective view of one molecule each of **2** and **3a** are depicted in Figs. 1 and 2, respectively. The copper(II) centers in **2** and **3a** are penta-coordinated and is bound by three nitrogen atoms of the anionic ligand in a meridional fashion, a monodentate acetate ion and a water molecule. Overall N_3O_2 coordination environment around the copper atom has a distorted square pyramidal geometry as is evident from the τ values that are lying in the range 0.01–0.05 in **2** and **3a** [27]. In general the Cu–N_D (N_D = diimide–N) is shorter than that of Cu–$N_{P/Q}$ (N_P = pyridine–N and N_Q = quinoline–N). The Cu–N_P lengths are comparable between those observed in **1** and **3a**, and within **3a** Cu–N_Q lengths are shorter than that of Cu–N_P. In **2**, each of the individual quinolinimide rings are planar and in a given ligand the dihedral angle between the two quinolinimide rings lies in the range 3.5–4.2°.

In **2**, packing reveals the presence of $\pi\cdots\pi$ interactions between the quinoline rings, with the non-bonded distances of C5⋯C13 3.32(2) Å and C9⋯C15 3.31(2) Å. The significant intermolecular H-bonding interactions present are O1⋯O6 2.913(12) Å, O2⋯O5 2.840(13) Å, O2⋯O7 2.906(9) Å. The packing diagram of **3** on viewing down the c-axis is shown in Fig. 3. It consists of separate layers made up of **3a** and **3b** units. The layers of **3a** and **3b** are segregated and commingled alternatively. The two layers are interlinked by hydrogen-bonding interactions viz., O3⋯O30 2.658(5) Å, O5⋯O26 2.895(7) Å, O8⋯O24 2.650(6) Å, O10⋯O20 2.899(7) Å, O13⋯O25 2.620(6) Å, O15⋯O23 2.944(7) Å. Within the **3a**-layers, the hydrogen-bonding that occur are O2⋯O15 2.937(6) Å, O5⋯O11 2.884(7) Å, O6⋯O10 2.872(7) Å, O7⋯O10 2.880(6) Å, O1⋯O15 2.877(7) Å. In addition $\pi\cdots\pi$ interactions exist between the quinoline rings with the non-bonded distances of C8⋯C30 3.361(9) Å and C12⋯C26 3.356(8) Å. Within the layers of **3b**, the molecules are isolated and no significant hydrogen-bonding interactions are found to occur.

The ORTEP plot of **bqcaH** is shown in Fig. 4. Two quinoline rings are planar and the packing diagram reveal the presence of $\pi\cdots\pi$ interactions. A cg⋯cg distance of 3.638(1) Å is present between the centers (cg) of two six-membered rings containing the nitrogen atom. Other significant non-bonded interactions present are C4⋯C4 3.291(2) Å, O2⋯C10, 3.142(2) Å, O1⋯C11 3.222(2) Å. The non-bonded distance between the two diimide oxygen atoms in **2** are O1⋯O1 2.741(9) Å, O5⋯O5 2.744(9) Å while that in **3a** are O1⋯O2 2.838(7) Å, O6⋯O7 2.765(9) Å, O11⋯O12 2.920(9) Å and that in **bqcaH** is O1⋯O2 2.911(2) Å. On comparison the values observed in **2** are comparable to those in **1** but shorter than that in **3a** and **bqcaH**.

3.3. Optical spectra and magnetism

Complexes **1**–**3** exhibit a characteristic strong intensity band for the $\nu_{(CO)}$ in the range 1705–1720 cm^{-1} and free ligands exhibit the same at around 1750 cm^{-1}. The characteristic feature of electronic spectra of **2** and **3** is the presence of a broad band in the visible region along with a shoulder on to its higher-energy side. These are of d–d transition in origin, the broad absorption and shoulder may be arising from the transition $d_{x^2-y^2}$ to d_{z^2} and $d_{x^2-y^2}$ to d_{xy}, respectively. The intra-ligand transitions occur in the 325–240 nm region. The room temperature μ_{eff} values are consistent with the presence of one unpaired electron in **2** and **3a**. The overall value of 1.97 B. M. for the co-crystal **3** may be due to the lesser magnetic moments shown by the dimeric copper(II) carboxylates [28]. The EPR spectra of **2** and **3** show the pattern of an axial spectrum with $g_{||} > g_{\perp} > 2$ signifying that the signals arise from **2** and **3a** and the odd electron being in the $d_{x^2-y^2}$ orbital. This observation also shows the **3b** is EPR silent under these conditions [29].

Table 2
Selected bond distance (Å) and angles (°).

*Compound **2***			
Cu1–N1	2.109(8)	Cu2–O6	2.293(10)
Cu1–N2	1.931(12)	Cu2–O7	1.974(9)
Cu1–O2	2.320(10)	C10–N2	1.346(12)
Cu1–O3	1.966(10)	C10–O1	1.204(12)
Cu2–N3	2.109(7)	C22–N4	1.334(11)
Cu2–N4	1.891(11)	C22–O5	1.245(13)
N1–Cu1–N1	161.1(4)	N3–Cu2–N3	159.9(4)
N1–Cu1–N2	81.0(2)	N3–Cu2–N4	80.7(2)
N1–Cu1–O2	89.3(3)	N3–Cu2–O6	90.1(2)
N1–Cu1–O3	99.4(2)	N3–Cu2–O7	100.0(2)
N2–Cu1–O2	103.4(4)	N4–Cu2–O6	112.4(4)
N2–Cu1–O3	157.9(5)	N4–Cu2–O7	155.3(5)
O2–Cu1–O3	98.7(4)	O6–Cu2–O7	92.3(4)
O1–C10–N2	128.9(11)	O5–C22–N4	129.7(11)
C10–N2–C10	121.1(13)	C22–N4–C22	120.2(13)
C10–N2–Cu1	119.4(6)	C22–N4–Cu2	119.6(6)
*Compound **3***			
Cu1–N1	2.088(5)	Cu3–O15	2.301(4)
Cu1–N2	1.966(5)	O1–C6	1.183(7)
Cu1–N3	2.035(5)	O2–C7	1.219(7)
Cu1–O3	1.969(4)	N2–C6	1.378(8)
Cu1–O5	2.300(4)	N2–C7	1.337(8)
Cu2–N4	2.062(5)	O6–C24	1.220(8)
Cu2–N5	1.966(5)	O7–C25	1.278(7)
Cu2–N6	2.089(5)	N5–C24	1.340(8)
Cu2–O8	1.967(4)	N5–C25	1.318(8)
Cu2–O10	2.278(4)	O11–C42	1.184(8)
Cu3–N7	1.969(5)	O12–C43	1.256(7)
Cu3–N8	1.951(5)	N8–C42	1.355(8)
Cu3–N9	2.142(5)	N8–C43	1.333(8)
Cu3–O13	1.965(4)		
N1–Cu1–N2	81.6(2)	N5–Cu2–O8	163.2(2)
N1–Cu1–N3	163.0(2)	N5–Cu2–O10	106.3(2)
N2–Cu1–N3	81.5(2)	N6–Cu2–O8	105.9(2)
N1–Cu1–O3	91.1(2)	N6–Cu2–O10	93.8(2)
N1–Cu1–O5	90.9(2)	O8–Cu2–O10	89.3(2)
N2–Cu1–O3	163.4(2)	N7–Cu3–N8	81.1(2)
N2–Cu1–O5	106.2(2)	N7–Cu3–N9	162.9(2)
N3–Cu1–O3	105.5(2)	N8–Cu3–N9	82.0(2)
N3–Cu1–O5	93.0(2)	N7–Cu3–O13	95.5(2)
O3–Cu1–O5	88.7(2)	N7–Cu3–O15	92.0(2)
N4–Cu2–N5	81.7(2)	N8–Cu3–O13	165.7(2)
N4–Cu2–N6	161.7(2)	N8–Cu3–O15	104.1(2)
N5–Cu2–N6	80.0(2)	N9–Cu3–O13	100.4(2)
N4–Cu2–O8	92.1(2)	N9–Cu3–O15	94.4(2)
N4–Cu2–O10	89.9(2)	O13–Cu3–O15	89.9(2)
bqcaH			
O1–C10	1.2138(14)	N2–C10	1.3783(18)
O2–C11	1.2127(15)	N2–C11	1.3721(19)
O1–C10–N2	125.13(14)	C10–N2–C11	129.56(11)
O2–C11–N2	125.13(14)		

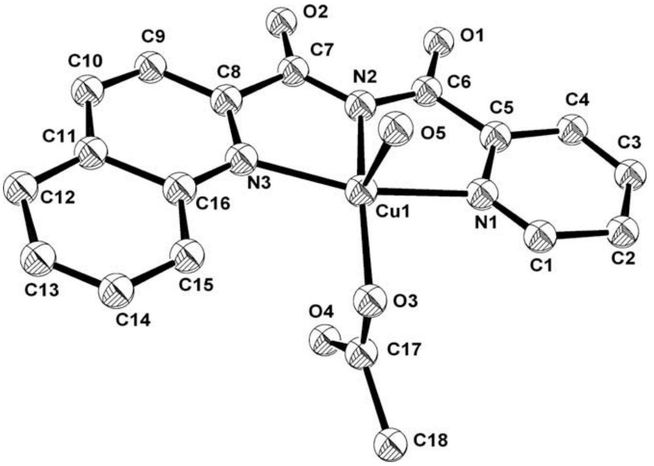


Fig. 2. ORTEP diagram (30% probability level) of **3a**. Hydrogen atoms are omitted for clarity.

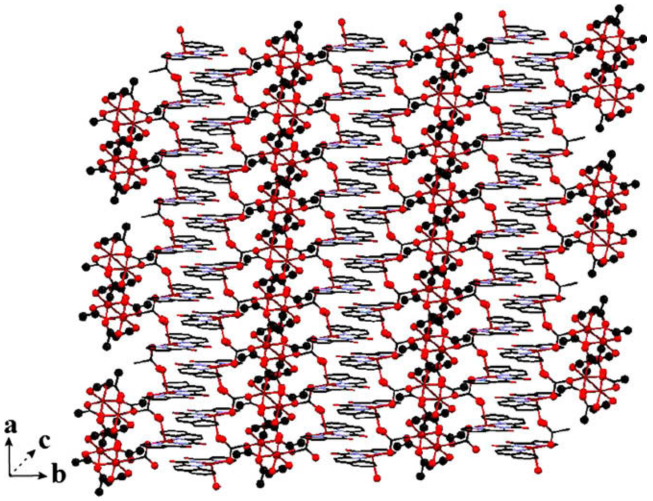


Fig. 3. Packing diagram of **3** on viewing down the *c*-axis.

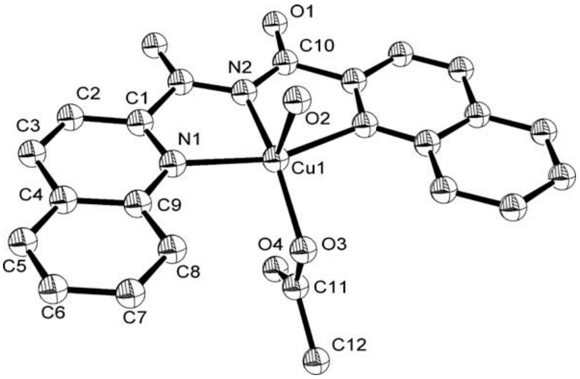


Fig. 1. ORTEP diagram (30% probability level) of **2**. Hydrogen atoms are omitted for clarity.

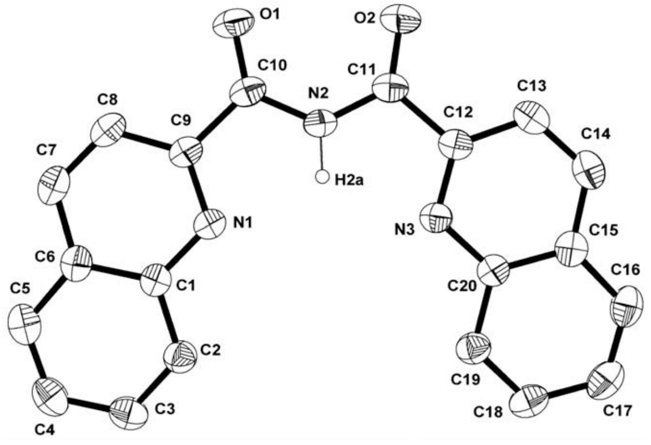


Fig. 4. ORTEP diagram (30% probability level) of **bqcaH**. Hydrogen atoms except H2a are omitted for clarity.

4. Conclusion

In summary, in hydrated ethanolic medium 2-(aminomethyl) substituted pyridine and quinoline were converted respectively to bis(2-pyridylcarbonyl)diimide and bis(2-quinolylcarbonyl)diimide species under mild conditions by stirring with copper(II) acetate. This reaction involve the oxidation of the methylene function as well as the formation of the bond between nitrogen and carbon in N–C(=O) through coupling and also show that the $-CH_2-$ group flanked by pyridyl/quinolyl group can be oxidized under mild conditions. The co-crystals of $[Cu(\textbf{pqca})(OAc)(H_2O)]_3[Cu_2(OAc)_4(EtOH)_2]_{1.5}$ were synthesized by stirring the ethanolic solution of the Schiff base [(2-pyridyl)-N-((2-quinolyl)methylene)methanamine] (**L1**) and with one equivalent of $Cu(OAc)_2 \cdot H_2O$, which involve the oxidation of both the imine and $-CH_2-$ groups. The free ligands were isolated as crystalline solids from the compounds **1–3** by extrusion of Cu^{2+} ion using $EDTA^{2-}$. In both **2** and **3a**, the copper(II) center has a distorted square pyramidal geometry and N_3O_2 coordination environment. The packing diagram of **3** consists of separate layers made up of **3a** and **3b** units that are segregated and commingled alternatively. Compounds having quinolyl group show the presence of π-stacking interactions.

5. Supplementary material

CCDC 284749, 754807, 754808 and 754809 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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References

[1] E.A. Lewis, W.B. Tolman, Chem. Rev. 104 (2004) 1047.
[2] J.M. Rowland, M.M. Olmstead, P.K. Mascharak, Inorg. Chem. 41 (2002) 2754.
[3] S.K. Padhi, V. Manivannan, Inorg. Chem. 45 (2006) 7994.
[4] C. Tejel, M.A. Ciriano, M.P. del Río, F.J. van den Bruele, D.G.H. Hetterscheid, N.T. Spithas, B. de Bruin, J. Am. Chem. Soc. 130 (2008) 5844.
[5] C. Tejel, M.A. Ciriano, M.P. del Rio, D.G.H. Hetterscheid, N.T. Spithas, J.M.M. Smits, D. de Bruin, Chem. Eur. J. 14 (2008) 10932.
[6] E.I. Lerner, S.J. Lippard, J. Am. Chem. Soc. 98 (1976) 5397.
[7] E.I. Lerner, S.J. Lippard, Inorg. Chem. 16 (1977) 1546.
[8] T. Kajiwara, T. Ito, J. Chem. Soc., Dalton Trans. (1998) 3351.
[9] T. Kajiwara, T. Ito, Angew. Chem., Int. Ed. 39 (2000) 230.
[10] A. Kamiyama, T. Noguchi, T. Kajiwara, T. Ito, Angew. Chem., Int. Ed. 39 (2000) 3130.
[11] A. Kamiyama, T. Noguchi, T. Kajiwara, T. Ito, Inorg. Chem. 41 (2002) 507.
[12] A. Kamiyama, T. Noguchi, T. Kajiwara, T. Ito, CrystEngCommun. 5 (2003) 231.
[13] R. Lescouëzec, J. Vaissermann, L.M. Toma, R. Carrasco, F. Lloret, M. Julve, Inorg. Chem. 43 (2004) 2234.
[14] T. Kajiwara, M. Nakano, Y. Kaneko, S. Takaishi, T. Ito, M. Yamashita, A. Igashira-Kamiyama, H. Nojiri, Y. Ono, N. Kojima, J. Am. Chem. Soc. 127 (2005) 10150.
[15] H.-R. Wen, C.-F. Wang, J.-L. Zuo, Y. Song, X.-R. Zeng, X.-Z. You, Inorg. Chem. 45 (2006) 582.
[16] A.M. Madalan, K. Bernot, F. Pointillart, M. Andruh, A. Caneschi, Eur. J. Inorg. Chem. (2007) 5533.
[17] F. Pointillart, K. Bernot, R. Sessoli, D. Gatteschi, Chem. Eur. J. 13 (2007) 1602.
[18] T. Kajiwara, I. Watanabe, Y. Kaneko, S. Takaishi, M. Enomoto, N. Kojima, M. Yamashita, J. Am. Chem. Soc. 129 (2007) 12360.
[19] V.K. Fulwa, R. Sahu, H.S. Jena, V. Manivannan, Tetrahedron Lett. 50 (2009) 6264.
[20] G.M. Sheldrick, SADABS, University of Göttingen, Göttingen, Germany, 1996.
[21] SMART and SAINT, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996.
[22] G.M. Sheldrick, SHELXS-97 and SHELXL-97, University of Göttingen, Göttingen, Germany, 1997.
[23] W.A. Chomitz, S.G. Minasian, A.D. Sutton, A. Arnold, Inorg. Chem. 46 (2007) 7199.
[24] J.W. Canary, Y. Wang, R. Roy, L. Que, H. Miyake, Inorg. Synth. 32 (1998) 70.
[25] M. Barquín, M.J.G. Garmendia, L. Larrínaga, E. Pinilla, M.R. Torres, Inorg. Chim. Acta 362 (2009) 2334.
[26] J.V. Folgado, E. Martínez-Tamayo, A. Beltran-Porter, D. Beltrán-Porter, Polyhedron 8 (1989) 1077.
[27] A.W. Addison, T.N. Rao, J. Reedijk, J. Van Rijn, G.C. Verschor, J. Chem. Soc., Dalton Trans. 2 (1984) 1349.
[28] M. Kato, H.B. Jonassen, J.C. Fanning, Chem. Rev. 64 (1964) 99.
[29] D.P. Dalal, S.S. Eaton, G.R. Eaton, J. Magn. Reson. 42 (1981) 277.