Note

Synthesis and characterization of bifunctional oligo-\(\alpha\)-aminopyridines and their copper(II) complexes

Hasanov Hasan\(^{a,b}\), Uan-Kang Tan\(^c\), Yu-Sheng Lin\(^a\), Chung-Chou Lee\(^a\), Gene-Hsiang Lee\(^a\), Tzu-Wei Lin\(^a\), Shie-Ming Peng\(^{a,b,*}\)

\(^a\) Department of Chemistry, National Taiwan University, 1 Sec, 4 Roosevelt Road, Taipei 106, Taiwan, ROC
\(^b\) Department of Chemistry, Academia Sinica, Taipei, Taiwan, ROC
\(^c\) Department of Chemical Engineering, Kuang Wu Institute of Technology, Taipei, Taiwan, ROC

Received 27 August 2002; accepted 4 February 2003

Abstract

The synthesis of two new bifunctional oligo-\(\alpha\)-aminopyridine ligands, \(N-(6-(6-[3-(6-amino-pyridin-2-ylamino)-phenylamino]-pyridin-2-yl)-4-methylbenzenesulfonamide (apppm) and \(N-(6-(6-[3-(6-bromo-pyridin-2-ylamino)-phenylamino]-pyridin-2-yl)-4-methylbenzenesulfonamide (bpppm), by double aminated couplings and Pd-catalysis is presented in this paper. NaNH\(_2\) was used as a critical base in the first step of the aminated coupling for synthesizing the key building block \(N-(6-bromo-pyridin-2-yl)-pyridine-2,6-diamine (bppd\) in 96% yield. Pyridine was then used in the second step of the aminated coupling for 4-toluenesulphonyl chloride and bppd. Finally, the monoamination was facilitated by the palladium-catalyzed Buchwald’s coupling reaction, and subsequently the corresponding metal complexes of these bifunctional ligands were constructed. The single-crystal X-ray crystallographic data of the complex \([Cu(apppm)(ClO_4)(H_2O)](ClO_4)\) (1), \([Cu(bpppm)(ClO_4)_2(H_2O)]_2(\text{CH}_3\text{CN})_3\) (3), and the related salt \([H(apppm)](ClO_4)_2\text{THF}\) (2), were prepared and characterized. In complex 1, Cu(II) coordinates with the three nitrogen atoms of the pyridine rings, with the oxygen atom of the \(p\)-toluenesulphonyl group, strongly with the oxygen of the water molecule, and weakly with the oxygen atom of the perchlorate anion, and shows a distorted octahedral geometry. However, in the complex 3, Cu(II) bonds to N(1), N(3), N(5), and N(7) of the ligand bpppm toughly and exhibits a twisted square planar geometry.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Oligo-\(\alpha\)-aminopyridine; Palladium-catalyzed; Distorted 6-coordinated octahedral geometry

1. Introduction

Organometallic reagents have often been utilized to catalyze the formation of carbon–nitrogen bond of heteroaromatics. Nitrogen-containing heteroaromatics have fascinating and versatile bonding properties, and their unique features have been well applied to organic chemistry, polymer chemistry, and supramolecular chemistry [1,2]. In particular, the growing applications of oligo-aminopyridines are observed in areas such as material science and industrial pharmacology [3]. Thus, the synthesis of oligo-aminopyridines has attracted many chemists’ interests recently. Using catalytic palladium complexes, Migita has synthesized aminopyridines [4], Buchwald’s [5] and Hartwig’s groups [6] have reported various primary and secondary amines with dihalides to give products in high yields, Kanbara has prepared high mass material poly(aryleneamines) [7], and Beletskaya has produced selective aryl-substituted polyamines [8]. It was noticed that bases and catalysts also play important roles, for examples, sterically hindered bases, LiO\(_t\)Bu, NaO\(_t\)Bu, and KO\(_t\)Bu; and the chelating biphoshine ligand, 1,1’-bis-(diphenylphosphino)-ferrocene (DPFF) [5e]; and the racemic catalyst 2,2’-bis(diphenylphosphonyl)-1,1’-binaphtyl (BINAP) [6b].

This work focuses on the synthesis of the bifunctional oligo-\(\alpha\)-aminopyridines, \(N-(6-(6-[3-(6-amino-pyridin-2-ylamino)-phenylamino]-pyridin-2-ylamino]-pyridin-2-ylamino]-pyridin-2-ylamino)-pyridin-2-
yI)-4-methylbenzenesulfonamide (apppm) and N-(6-{6-
[3-(6-bromo-pyridin-2-ylamino)-phenylamino]-pyridin-
2-ylamino}-pyridin-2-yl)-4-methylbenzenesulfonamide
(bpppm), and the structure–property relationship of the
corresponding Cu(II) complexes [Cu(apppm)(ClO₄)₂-
(H₂O)](ClO₄)·2THF (1), and [Cu(bpppm)](ClO₄)₂-
(H₂O)₃/₈(CH₃CN)½/₃ (3). The reason of choosing copper
metal was originated from the need to understand the
copper proteins [9], and bifunctional oligo-α-aminopy-
ridines were selected for their structural features to
learn the multibinding capabilities [10–12]. Based on the
literature survey, the coordination study of Cu(II)
complexes with the aminopyridines have illustrated
variety of geometries, such as tetrahedral [10a], square
planar [10b], square pyramid [10b], trigonal planar [10g],
and distorted octahedral [10h].

In order to obtain more information of the coordi-
nated geometries of Cu(II) and bifunctional oligo-
α-amino pyridines, we have synthesized two new ligands,
apppm and bpppm. Two new metal complexes, 1 and 3,
and its related salt [H(apppm)(ClO₄)·THF (2) were
synthesize and characterized in details with single X-
ray crystallographic analysis.

2. Experimental

2.1. Chemicals and general procedures

Benzene, THF, and toluene were pre-dried, and
freshly distilled from sodium suspension. All starting
chemicals were purchased from Aldrich. All procedures
were carried out in Ar and using standard high-vacuum
techniques.

2.2. Physical measurements

The infrared spectra were recorded on a Nicolet
Fourier Transform IR MAGNA-IR 500 spectrophot-
ometer in the range of 500–4000 cm⁻¹ using KBr disk
technique. UV–Vis spectra were recorded on a
Hewlett–Packard (HP) 8453 spectrophotometer. Max-
imum absorptions were recorded (in CH₃OH) and listed
in the form of λmax (nm) [ε (M⁻¹ cm⁻¹)]. The ¹H and
¹³C NMR spectra were measured on a Bruker Advance-
400 MHz spectrometer. Elemental analysis was per-
formed on a Perkin–Elmer CHN analyzer 2400. Fast
atom bombardment mass (FAB MS) spectra were
obtained on a JEOL-SX 102A mass spectrometer with
m-nitrobenzyl alcohol (m-NBA) as the matrix.

2.3. The preparation of ligands

2.3.1. The synthesis of N-(6-bromo-pyridin-2-yl)-
pyridine-2,6-diamine (bppd)

To a 2 L two-necked round-bottomed flask, 2,6-
diaminopyridine (20.00 g, 0.18 mol), sodium amide
(11.91 g, 0.31 mol), and anhydrous toluene (600 mL)
were added. The mixture was stirred and refluxed for 24
h. Subsequently, dibromopyridine (36.18 g, 0.15 mol) in
toluene (300 mL) was added drop by drop to this
solution over 1 h, and the whole solution was refluxed
for another 48 h. The hot reaction mixture (85 °C)
was quenched by water (300 mL, ~25 °C) and then
extracted with hot toluene (4 × 1 L), and the combined
organic solution was dried over anhydrous MgSO₄
and filtered. The filtrate was concentrated in vacuo, and
the residue was purified by flash chromatography (silica gel
60–300 mesh) to obtain the desired product bppd as
white solids in 96% yield (38.85 g, m.p. 112 °C) and 2% yield of side product bbppd (see Section 2.3.2).

C, 45.41; H, 3.21; N, 20.94%. IR (KBr): 3448, 3310,
3198, 1635, 1562, 1516, 1352, 1418, 1155, 1122 cm⁻¹.

2.3.2. The synthesis of N,N’-bis-(6-bromo-pyridin-2-yl)-pyridine-
2,6-diamine (bbppd)

It is a side product with an optimized yield of 40%
(0.64 g) from another trial where 2,6-diaminopyridine
(5.00 g, 0.05 mol) and dibromopyridine (21.71 g, 0.09
mol) were employed under the previous described
experimental conditions. Anal. Calc. for C₁₁H₁₁Br₂N₄:
C, 42.76; H, 2.61; N 16.63. Found: C, 42.94; H, 2.47; N,
16.38%. IR (KBr): 3254, 3167, 3066, 1609, 1514 cm⁻¹.

¹H NMR (400 MHz, Me₂SO-d₆): δ 9.54 (s, 1H, NH),
8.04 (d, 1H, aromatic H₃), 7.51 (t, 1H, aromatic H₅),
7.28 (t, 1H, aromatic H₄), 6.97 (d, 1H, aromatic
H₆), 6.56 (d, 1H, aromatic H₅), 5.99 (d, 1H, aromatic
H₆), 5.78 (s, 2H, NH₂). ¹³C NMR (100 MHz, Me₂SO-
d₆): δ 158.0, 154.5, 152.3, 139.8, 151.6, 139.4, 119.2,
109.7, 101.4, 100.7. MS (FAB) [m/z]: [265 (M + 1)⁺].
UV–Vis (CH₃OH): 329 (ε = 3.85 × 10⁴), 270 (ε = 3.05 ×
10⁴), 229 (ε = 2.21 × 10⁴), 206 nm (ε = 4.43 × 10⁴).

2.3.3. The synthesis of N-[3-(3-bromo-phenylamino)-
phenyl]-4-methyl-benzenesulfonamide (bppm)

To a 500 mL two-necked round-bottomed flask, a
solution of bppd (7.40 g, 28 mmol) in anhydrous
pyridine (20 mL) was loaded, then 4-toluenesulphonyl
chloride (10.64 g, 55.82 mmol) in pyridine (20 mL) was
loaded, then 4-toluenesulphonyl chloride (10.64 g, 55.82 mmol) in pyridine (20 mL) was
added to this solution, and the mixture was stirred at room temperature (r.t.) for 2 h. To this reaction mixture, 20% NaOH was added dropwise until the pH reached 9. The crude product was extracted with EtOAc (3 × 100 mL) and then was washed with water (3 × 100 mL). The water layer was extracted with EtOAc (2 × 100 mL) again. The combined organic layer was dried over anhydrous MgSO₄ and allowed to stand overnight. After filtration, the solution was concentrated in vacuo to obtain the desired compound bppm in 95% yield (11.11 g) without further purification. *Anal. Calc. for C₂₉H₂₃BrN₈O₂S: C, 53.73; H, 3.81; N, 18.57. Found: C, 53.74; H, 3.81; N, 18.50%. IR (KBr): 3449, 3348, 3153, 1636, 1575, 1444, 1366, 1319, 1155 cm⁻¹. ¹H NMR (400 MHz, Me₂SO-d₆): δ 10.74 (s, 1H, SO₂NHa), 9.77 (s, 1H, NH), 9.10 (s, 2H, NH₂), 8.15 (d, 1H, Hg), 7.81 (d, 2H, Hf), 7.53 (m, 6H, Hgₘ+₁₋₉₊₁₋₉). 7.32 (d, 2H, Hm), 7.04 (m, 3H, Hₙ+₁₋₉₊₁₋₉), 6.87 (d, 1H, Hg), 6.47 (d, 1H, Hf), 2.49 m (s, 3H, CH₃). MS (FAB) [m/z]: [605 (M+1)⁺]. UV–Vis (CH₃OH): 374 (ε = 3.23 × 10⁴), 341 (ε = 3.30 × 10⁴), 256 (ε = 2.96 × 10⁴), 204 nm (ε = 3.61 × 10⁴).

2.4. The preparation of Cu(II) complexes 1, 2, and the related salt 2

2.4.1. The synthesis of [Cu(apppm)(ClO₄)₂]·2THF (1)

Apppm (0.10 g, 0.22 mmol), Cu(ClO₄)₂·6H₂O (0.13 g, 0.34 mmol), and THF (30 mL) were placed in a round-bottomed flask (50 mL). The mixture was stirred at r.t. for 2 h. A violet powder product was isolated by filtration in 80% yield (0.16 g). The single crystal of 1 was obtained from the mixed DMF–THF/Er₂O₂ by slow diffusion techniques. *Anal. Calc. for C₃₀H₃₉Cl₂Cu₇N₉O₁₃S: C, 41.28; H, 4.47; N 11.24. Found: C, 41.35; H, 4.40; N, 11.08%. IR (KBr): 3341, 3241, 3153, 1636, 1575, 1454, 1132, 1085 cm⁻¹. MS (FAB) [m/z]: [1119 (2apppm+2Cu²⁺+2ClO₄⁻)]. UV–Vis (CH₃OH): 381 (ε = 7.654 × 10³), 340 (ε = 2.27 × 10⁴), 247 (ε = 1.60 × 10⁴), 231 (ε = 1.61 × 10⁴), 204 nm (ε = 2.23 × 10⁴).

2.4.2. Synthesis of [H(apppm)]·[ClO₄]·THF (2)

To a round-bottomed flask (50 mL), apppm (0.10 g, 0.22 mmol), 70% of HClO₄ (0.03 mL, 0.35 mmol), and THF (30 mL) were loaded. This reaction mixture was stirred at r.t. for 2 h. The protonated compound 2 was isolated by filtration of the THF solution in 80% yield (0.10 g). The crystal of 2 was obtained from THF/
hexane system. Anal. Calc. for C_{26}H_{30}Cl_{2}N_{2}O_{5}S: C, 50.32; H, 4.84; N 15.80. Found: C, 50.41; H, 4.80; N, 15.69%. IR (KBr): 3523, 3429, 1615, 1461, 1152, 1105 cm\(^{-1}\). MS (FAB) \([m/z]\): \[\{619 \ (apppm \ + \ Cu^{2+} \ + \ ClO_4^-)\}\].

2.4.3. Synthesis of [Cu(bpppm)](ClO\(_4\))\(_2\)·(H\(_2\)O)\(_{3}\)·(CH\(_3\)CN)\(_{13}\)·(CH\(_3\)CN)\(_{13}\) (3)

To a round-bottomed flask (50 mL), bpppm (0.10 g, 0.16 mmol) and Cu(ClO\(_4\))\(_2\)·6H\(_2\)O (0.09 g, 0.24 mmol), and THF (15 mL) were loaded. The mixture was stirred at r.t. for 2 h. The copper complexes were isolated by filtration in 75% yield (0.12 g). The reddish-purple crystal 3 was obtained from CH\(_3\)CN/ether by diffusion techniques. Anal. Calc. for C\(_{78.67}\)H\(_{27.33}\)Br\(_5\)N\(_{8.33}\)O\(_{11.67}\)S: C, 36.50; H, 3.00; N, 12.82. Found: C, 36.69; H, 3.00; N, 12.54%. IR (KBr): 3415, 3073, 1649, 1454, 1226, 1119 cm\(^{-1}\). MS (FAB) \([m/z]\): \[766 \ (bpppm \ + \ Cu^{2+} \ + \ ClO_4^-)\]. UV–Vis (CH\(_3\)OH): 394 (\(\varepsilon = 3.32 \times 10^3\)), 350 (\(\varepsilon = 1.21 \times 10^3\)), 335 (\(\varepsilon = 1.12 \times 10^4\)), 235 (\(\varepsilon = 1.08 \times 10^4\)), 204 nm (\(\varepsilon = 5.89 \times 10^3\)).

2.5. Crystallography

Data collection for ligand bppd and compound 1 were carried out on a Siemens SMART diffractometer with a CCD detector (150 K), on a NONIUS CAD4 diffractometer (295 K) for compound 2, and on a KappaCCD (150 K) for compound 3. All measurements were carried out under Mo K\(_\alpha\) radiation (\(\lambda = 0.71073\) Å), and the cell parameters were listed in Table 2. The structures of bppd, 1, 2 and 3 were identified by direct methods and refined with full-matrix least-square methods on \(F^2\) by SHELXL-97 (G.M. Sheldrick, 1997, University of Göttingen, Germany). All of the nonhydrogen atomic positions were located in different Fourier maps and refined anisotropically. The hydrogen atoms attached to nitrogen atoms were located and refined isotropically. The rest of hydrogen atoms attached to the carbon atoms were placed in their geometrically generated positions.

3. Results and discussion

3.1. The synthesis of ligands bppd and bbppd

Ligand bppd was the key building block to prepare our final target ligands apppm and bpppm. The synthesis of ligand bppd was first tried via palladium-catalyzed amination of dianimopyridine and dibromo-pyridine. However, the attempt was not successful, and only unexpected polymers [7] or the \(\beta\)-elimination side products were obtained as reported previously [56]. The failure may be due to both of the starting materials being active under the reaction conditions. Less than 40% of bppd was obtained when various bulky bases, such as NaO\(_{2}\)Bu or KO\(_{2}\)Bu, and chelating agents like BINAP, DPPP, and 1,1'-bis(diphenylphosphino)ferrocene were added into the reaction mixture in the absence of palladium catalyst. However, the yield of bppd was optimized to 96% by using NaN\(_2\)H\(_2\) as a base in the first aminated step after many trials (Scheme 1). It may be noted that since NaN\(_2\)H\(_2\) (pK\(_a\) ~ 33) is a stronger base than KO\(_{2}\)Bu (pK\(_a\) ~ 19), the formation of products favor to facilitate by employing NaN\(_2\)H\(_2\).

Compound bbppd, a side product (2%) from the first aminated step with NaN\(_2\)H\(_2\) treatment, is a potential bifunctional oligo-\(\alpha\)-aminopyridine ligand. The yield was optimized to achieve 40% under 1:2 molar ratio of 2,6-dianimopyridine and 2,6-dibromopyridine. Ligand bbppd has a C\(_2\) fold symmetry, thus only half carbons of the skeleton were observed in the \(^1\)\text{H} NMR.

3.2. The crystal stucture and properties of the key building block bppd

The single crystal of compound bppd was obtained from a mixture of ethyl acetate and hexane by the layer diffusion technique. Four pairs of the intermolecular hydrogen bondings were observed through N4···N1A (3.004 Å), N3···N2A (3.571 Å) and N2···N3A (3.571 Å), N1···N4A (3.004 Å) in sequential order within a dimer (Fig. 1). Two middle hydrogen bondings are longer than the terminal ones because the middle ones have more constraint in packing formation. There are two other intermolecular hydrogen bondings observed: one was constructed through the hydrogen atom of the ‘amine end’ to the ‘Br atom’ of another molecule (bppd) at the adjacent layer, and the other from the ‘Br atom’ to the ‘NH\(_2\) end’ of another molecular (bppd) at the same surface.

It was also observed that all (bppd) molecules possessed the head-to-tail packing, and there was no distinct \(\pi–\pi\) interaction (it usually occurs at \(~3.4\) Å) between the pyridine planes in the layered structure (Fig. 2). In the case of bppd, the dihedral angle between Br–pyridine and NH\(_2–\)pyridine is 32.89°, and both Br–pyridine and NH\(_2–\)pyridine can form the ‘least square planes’ individually. The ‘least square plane’ for Br–pyridine is 4.20 Å (dihedral angle = 0°), and for NH\(_2–\)pyridine is 2.47 Å (dihedral angle = 0°).
transition. In the IR spectra of bppd, several N–H peaks were observed from a solid KBr pallet (3448, 3310, 3199, 3108, and 3093 cm⁻¹); however, they became only two peaks in CH₂Cl₂ solution (3505 and 3403 cm⁻¹) in the region of 3000–3600 cm⁻¹. The previous observation is due to different degrees of hydrogen bonding influences to the N–H stretches. It is consistent with that there are two sets (four pairs) of
intermolecular hydrogen bondings exhibit within a dimer from the crystallographic evidence (Fig. 1).

3.3. The synthesis and properties of the bifunction oligo-α-aminopyridine ligands apppm and bpppm

Ligands apppm and bpppm were obtained via several steps starting from the key building block bppd. The purposes of introducing a p-toluenesulphonyl substituent (Ts) into the ligands apppm and bpppm, is not only for protecting the end amino group of bppd from self-dimerization during the second aminated step, but also for stabilizing the formation of metal complex 1 by direct coordinating through the oxygen atom in the Ts group (Scheme 1). It is different from the previously reported case in which a direct formation of nitrogen–metal bond of the similar ligand is observed in [Cu3L2]− [12]. Sulphonylation of ligand bppd yielded the quantitative ligand bppm in the second step of the aminated coupling. The ligand bppm was used next for apppm synthesis without further purification.

The bifunctional oligo-α-aminopyridine apppm was obtained in a yield of 60% by the Buchwald’s palladium-catalyzed coupling of bppm and 2,6-diaminopyridine. To get the higher yield in apppm, it was critical to avoid the formation of the side products, such as polymers and the elimination products, by not mixing Pd2(dba)3, BINAP and NaO'Bu at the very beginning of the reaction. Based on the NMR study, strong intermolecular hydrogen bonding was observed in ligand apppm, the very broad peaks (δ = 8.8–9.5) were recorded. The chemical shifts of these peaks were subjected to change in different concentrations of sample in d6-DMSO. However, this feature was totally absent in the compounds bppd, bppm and bpppm. Both bppd and apppm showed strong hydrogen bondings and might serve as potential building blocks for the self-assembling materials [13], supramolecular tubes [14], and artificial ion channels [15].

In a similar approach, the bifunctional oligo-α-aminopyridine bpppm was obtained in a relatively low yield (40%) by coupling of bppd and bppm in similar palladium-catalyzed Buchwald’s conditions. Attempts to improve the yields were not successful by manipulating the substrate ratios, or catalytic systems and solvents.

3.4. The preparation and crystallographic properties of copper complexes 1, and 3, and the salt 2

The 6-coordinated copper complex 1 was synthesized by mixing Cu(ClO4)2·6H2O and apppm in a molar ratio 1.5:1, and its violet single crystal was obtained from the mixed solvent DMF–THF/Et2O by slow diffusion techniques. The protonated salt 2 was obtained by mixing HClO4 and apppm in a molar ratio of 1.6:1, and its crystal was obtained from the THF/hexane by similar diffusion techniques (Scheme 1). The synthetic route for the compound 3 is illustrated in Scheme 2. The reddish-violet crystal of copper complex 3 could not be obtained from the previously reported DMF–THF/Et2O system; however, it could be generated from CH3CN/ether system by the diffusion techniques.

The single-crystal X-ray crystallographic analysis of compound 1 reveals that the Cu(II) is coordinated with the three nitrogen atoms of pyridine moieties with the distance of 1.965(5), 2.042(5), 2.061(5) Å, respectively. Besides, Cu(II) in 1 is also coordinated: (i) with an oxygen atom of the ligand apppm [2.377(4) Å]; (ii) strongly with one oxygen of the water molecule [1.951(5) Å]; and (iii) weakly with the oxygen atom of perchlorate anion [2.511(2) Å] (Fig. 3). The electronic configuration of the Cu(II) of compound 1 was [Ar]3d9, and this
molecule showed a slightly distorted octahedral geometry resulting from the strong interactions between the metal center and both of water and the perchlorate [16]. In addition, the anti—anti conformation of N(2)–N(3)–N(4) and the twisted syn—anti conformation of N(4)–N(5)–N(6) played important roles as well. The geometry of compound 1 is different from the tetrahedral [10a], square planar [10b], square pyramid [10b], or trigonal planar [9g] ones for most of commonly related complexes. Based on the packing structure of compound 1, it is known that another ClO$_4^-$ and two THF joined the formation of this particular molecular cell, and only parts of hydrogen bondings are depicted in Fig. 4 for the reason of legibility.

As indicated by the structures of compound 2 (Fig. 5), the protonated position was performed at the N(2), and the distance of the hydrogen bonding was reported in Table 1. Besides, the conformation of compound 2 for N(2)–N(3)–N(4) is anti—anti, and that of N(4)–N(5)–N(6) is anti—syn. The crystal packing of compound 2 is shown in Fig. 6. The hydrogen bondings of this compound were not all drawn to avoid the complication for legibility reason.

The crystal structure for Cu(II) in the compound 3 displayed surprisingly a twisted square planar geometry despite of the great similarities between the ligands apppm and bpppm. This may be due to all nitrogen atoms in bpppm have the trans—trans conformation so that the backbone structure of the ligand without any skewness is most favored. The bond lengths between Cu(1)–N(1), Cu(1)–N(3), Cu(1)–N(5), and Cu(1)–N(7) are 1.985, 1.952, 1.959, 1.972 Å, respectively basing on the X-ray structure of compound 3 as shown in Fig. 7. The detailed comparisons of all hydrogen bondings for the compounds 1–3 are shown in Table 1, where only compound 2 possessed two intramolecular hydrogen bondings. For comparisons, the X-ray crystallographic data of the compounds bppd, 1, 2, and 3 are listed in the Table 2, where the space groups of bppd, 1, and 2 are monoclinic, and that of 3 is triclinic.
4. Conclusion

This work presents the synthesis of the bifunctional oligo-\(\alpha\)-aminopyridines with optimized yields by employing the base-induced reactions (NaNH\(_2\) and pyridine) and the Buchwald’s palladium-catalyzed coupling. The compounds 1–3 and the ligands bppd and apppm have all shown intermolecular hydrogen bondings. The single X-ray crystallographic data of the new bifunctional oligo-\(\alpha\)-aminopyridine metal complexes, [Cu(apppm)(ClO\(_4\))(H\(_2\)O)](ClO\(_4\))·2THF (1) and [Cu(bpppm)](ClO\(_4\))\(_2\)·(H\(_2\)O)\(_{5/3}\)·(CH\(_3\)CN)\(_{1/3}\) (3), were prepared and characterized. Based on the X-ray diffraction study of these copper complexes, a distorted octahedral geometry in 1 and a twisted square planar geometry in 3.

![Fig. 5. The ORTEP structure and atom labeling of compound 2.](image5)

![Fig. 6. The crystal packing of compound 2.](image6)

![Fig. 7. The ORTEP structure of the cation in compound 3.](image7)

Table 1

<table>
<thead>
<tr>
<th>Types of bonding</th>
<th>1 (Cu(apppm)(ClO(_4))(H(_2)O))(ClO(_4))·2THF)</th>
<th>2 (H(apppm))(ClO(_4))·THF)</th>
<th>3 (Cu(bpppm)](ClO(_4))(_2)·(H(<em>2)O)(</em>{5/3})·(CH(<em>3)CN)(</em>{1/3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermolecular</td>
<td>N2·N4 (2.695 Å)</td>
<td>N4·O11 (ClO(_4)) (2.556 Å)</td>
<td>N6·O11 (ClO(_4)) (2.986 Å)</td>
</tr>
<tr>
<td></td>
<td>(H(_2)O)O3·O12 (THF) (2.659 Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(H(_2)O)O3·O13 (THF) (2.655 Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ClO(_4))O4·N6 (ligand) (3.319 Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ClO(_4))O5·N3 (ligand) (2.954 Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ClO(_4))O6·N3 (ligand) (3.111 Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ClO(_4))O6·N5 (ligand) (3.222 Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ClO(_4))O7·N5 (ligand) (2.943 Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ClO(_4))O9·N7 (ligand) (2.974 Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intramolecular</td>
<td>(ClO(_4))O4·N3 (3.029 Å)</td>
<td>(ClO(_4))O4·N1 (3.230 Å)</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 8. The ORTEP structure and atom labeling of compound 2.](image8)
Table 2
The crystallographic data of compounds bppd, 1, 2 and 3

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ligand</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bppd</td>
<td>[Cu(apppm)(ClO4)(H2O)]·(ClO4)·2THF</td>
<td>[H(apppm)]·(ClO4)·THF</td>
<td><a href="ClO4">Cu(bpppm)</a>2·(H2O)5·(CH3CN)1/3</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C10H8BrN4</td>
<td>C26H30Cl2CuN4O3S</td>
<td>C26H30Cl2CuN4O3S</td>
<td>C27H32N3O11·BrCl2CuN4·3O11·6.5S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>265.12</td>
<td>872.18</td>
<td>620.08</td>
<td>909.66</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>150</td>
<td>150</td>
<td>295</td>
<td>150</td>
</tr>
<tr>
<td>Radiation λ (Å)</td>
<td>0.7107</td>
<td>0.7107</td>
<td>0.7107</td>
<td>0.7107</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
<td>P1</td>
<td>Cc</td>
<td>P1</td>
</tr>
<tr>
<td>Dimension (mm3)</td>
<td>0.30 × 0.25 × 0.20</td>
<td>0.30 × 0.15 × 0.03</td>
<td>0.25 × 0.12 × 0.05</td>
<td>0.23 × 0.15 × 0.15</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>24.8531(2)</td>
<td>9.5897(1)</td>
<td>22.922(5)</td>
<td>12.079(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>5.69390(10)</td>
<td>11.4034(1)</td>
<td>10.205(2)</td>
<td>17.5632(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>16.4191(2)</td>
<td>17.5163(1)</td>
<td>12.795(3)</td>
<td>24.9333(5)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>72.8798(9)</td>
</tr>
<tr>
<td>β (°)</td>
<td>120.512</td>
<td>104.696(1)</td>
<td>100.69(3)</td>
<td>86.8801(9)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>87.4533(7)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>2001.73(5)</td>
<td>1852.83(3)</td>
<td>2941.1(10)</td>
<td>5042.00(16)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>2</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>(D_{\text{calc}}) (g cm(^{-3}))</td>
<td>1.759</td>
<td>1.563</td>
<td>1.400</td>
<td>1.798</td>
</tr>
<tr>
<td>(\mu) (mm(^{-1}))</td>
<td>4.076</td>
<td>0.863</td>
<td>0.257</td>
<td>2.136</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>SMART CCD</td>
<td>SMART CCDb</td>
<td>NONIUS CAD4</td>
<td>KappaCCD</td>
</tr>
<tr>
<td>(\theta) Range (°)</td>
<td>1.90–27.50</td>
<td>1.79–26.38</td>
<td>1.81–25.00</td>
<td>1.26–25.00</td>
</tr>
<tr>
<td>(T_{\text{min}}/T_{\text{max}})</td>
<td>0.4031/0.4861</td>
<td>0.6776/0.8621</td>
<td>0.8703/0.9527</td>
<td>0.6570/0.738</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2312</td>
<td>7045 (R_{int} = 0.0369)</td>
<td>2592</td>
<td>17724 (R_{int} = 0.0777)</td>
</tr>
<tr>
<td>Goodness-of-fit on (I^2)</td>
<td>1.066</td>
<td>1.053</td>
<td>1.009</td>
<td>1.035</td>
</tr>
<tr>
<td>(R_{I}^2/\sigma(R_{I})) [(I &gt; 2\sigma(I))]</td>
<td>0.0203/0.0549</td>
<td>0.0626/0.1474</td>
<td>0.0519/0.1340</td>
<td>0.0913/0.2320</td>
</tr>
</tbody>
</table>

\(^a\) The functions minimized during least-squares cycles were \(R = \Sigma \left| F_o - |F_c|/\Sigma |F_o| \). \(R_{I}^2 = (\Sigma w(F_o^2 - F_c^2)^2)/\Sigma (w(F_o^2)^2)^{1/2}.\)

5. Supplementary material

Crystallographic data for the structural analysis have been registered in the Cambridge Crystallographic Data Center, CCDC Nos. 178279–81, for compounds bppd, 1, and the salt 2, respectively and CCDC No. 199290, for the compound 3. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the National Science Council and the Ministry of Education of the Republic of China for the financial supports.

References


