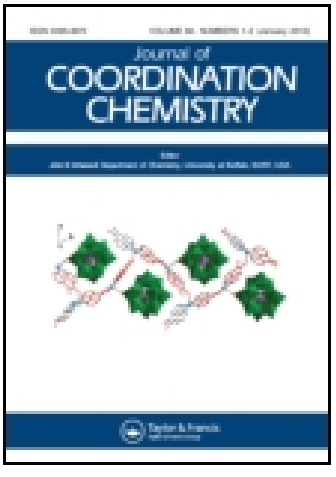

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Preparation and characterization of 4-amino-2-anilinopyridine and its chlorodiruthenium(III,II) complex

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Accepted author version posted online: 28 Aug 2014.Published online: 23 Sep 2014.

To cite this article: Naga V. Naidu, Hadi Arman, Yuanjian Deng & Xin Wei (2014) Preparation and characterization of 4-amino-2-anilinopyridine and its chlorodiruthenium(III,II) complex, Journal of Coordination Chemistry, 67:18, 3006-3017, DOI: 10.1080/00958972.2014.957199

To link to this article: http://dx.doi.org/10.1080/00958972.2014.957199

Journal of Coordination Chemistry, 2014
Vol. 67, No. 18, 3006–3017, http://dx.doi.org/10.1080/00958972.2014.957199

Preparation and characterization of 4-amino-2-anilinopyridine and its chlorodiruthenium(III,II) complex

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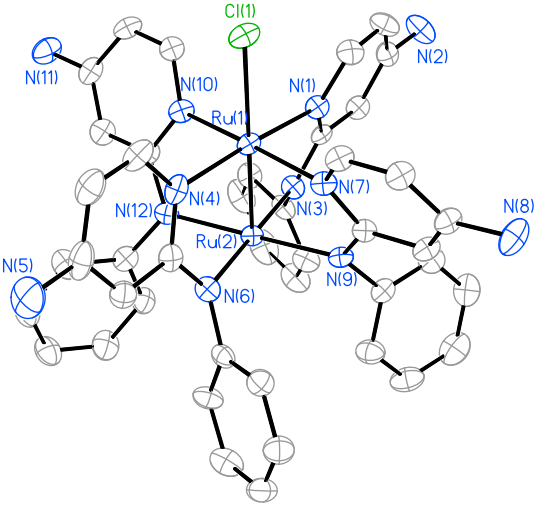
(*Received 19 March 2014; accepted 21 July 2014*)



A new bridging agent, 4-amino-2-anilinopyridine (aap), was synthesized and used as an equatorial ligand in the preparation of a diruthenium complex (4,0) $Ru_2(aap)_4Cl$. Both the ligand and the diruthenium complex were characterized by thermal analysis, MALDI-TOF mass spectrometry, IR and NMR (^1H and ^{13}C) spectroscopy, and X-ray crystallography. The structural analysis revealed that the complex existed as a (4,0) isomer, in which the amino group on the pyridyl moiety was not involved in chemical bonding.

Keywords: 4-Amino-2-anilinopyridine; Diruthenium complex; X-ray; Thermal analysis; NMR

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1. Introduction

Diruthenium complexes have been widely studied due to their catalytic properties [1], potential anticancer activity [2], and rich redox chemistry [3–8]. One group of mixed-valent diruthenium complexes with a general formula $Ru_2(L_e)_4(L_a)_x$ (where L_e is an equatorial chelating agent, L_a is an axial ligand, and x = 1 or 2) has been extensively investigated [5–13]. A paddle wheel like structure of the diruthenium complex is shown in chart 1. Common equatorial ligands include acetate [9], anilinopyridinate (ap) and substituted-ap anions [10], N,N′-dimethylbenzamidinate (dmba) [11], N,N′-diphenylformamidinate (dpf) [12], and 2,2′-dipyridylamide (dpa) [13]. Studies have shown that axial ligands have greater impact on the molecular structures and redox properties of the diruthenium complexes, whereas variations of the equatorial ligands have more subtle effects on the redox properties [10–13]. Most of the studies on diruthenium complexes that contain ap or substituted-ap bridging ligands have focused on the influence of aniline substitution on the structure and chemical properties of the complexes. Since ap is an unsymmetrical ligand, diruthenium complexes with four identical ap ligands may exist in up to four different isomeric forms, which are commonly designated as the (4,0), (3,1), (2,2)-cis, and (2,2)-trans conformations depending on whether the pyridyl nitrogen (N_p) and the aniline nitrogen (N_a) of different ap ligands are on the same plane or not. Recently a new diruthenium complex containing the pyridyl substitution with a methyl group on the *para* position has been reported [14]. This complex was determined to be a (3,1) isomer. We are intrigued by the fact that methyl is a weak electron-donating group and what would happen if the pyridyl substitution involves a stronger electron-donating group such as an amino group. Also, adding an amino group to the pyridyl moiety further expands the functionality of the complex. It is thus anticipated that fine tuning the molecular structure and subsequently the physiochemical properties would become possible. Indeed, replacing the methyl group attached to the pyridyl moiety with an amino group, resulted in the formation of a (4,0) isomer rather than the (3,1) isomer, as reported [14].

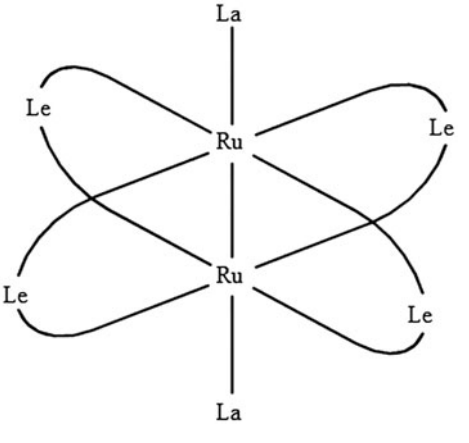

Chart 1. Schematic representation of a paddle like structure of diruthenium complexes.

2. Experimental

2.1. *Materials and measurements*

ACS grade aniline, 4-amino-2-chloropyridine (acp), lithium chloride, ruthenium(III) chloride trihydrate, isopropanol, acetonitrile, trifluoroacetic acid, methanol, and dichloromethane were purchased from Sigma-Aldrich Chemical Co. Deuterated DMSO-d_6 was supplied by Cambridge Isotope Laboratories, Inc. Sinapinic acid used as the matrix in MALDI-MS analysis was purchased from ProteoChem Inc. All the chemicals were used as received. The precursor $Ru_2(CH_3COO)_4Cl$ was synthesized according to the reported method [15].

Melting point was determined by differential scanning calorimetry (DSC) using a Q2000 DSC (TA Instruments) at a heating rate of 20 °C min^{-1} with N_2 purge (flow rate: 50 mL min^{-1}). Approximately, 10 mg samples were contained in crimped aluminum DSC pans and lids. Thermogravimetric analysis (TGA) was performed on a Q5000 IR TGA (TA Instruments) at a heating rate of 20 °C min^{-1} in air (air flow rate: 25 mL min^{-1}). In a platinum TGA pan, 5–10 mg samples were placed. Mass spectra were obtained with Bruker Daltonics Microflex MALDI-TOF mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm). The matrix was prepared by adding a solution of sinapinic acid and trifluoroacetic acid into a mixture of acetonitrile, methanol, and deionized water. Then the analyte was dissolved in the matrix, spotted on the target plate, and dried under a stream of nitrogen. The MALDI-TOF was validated using acp as the standard prior to sample analysis. ^1H and ^{13}C NMR spectra were obtained on a JEOL 400 MHz spectrometer. The NMR experiments on the aap ligand were conducted in deuterated dimethylsulfoxide (DMSO-d_6), on which signals were locked. The NMR spectra of the starting materials (acp and aniline) were also collected for the purpose of validation. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced to the instrument's locked values for DMSO-d_6 at 2.50 and 39.52 ppm, respectively [16].

2.2. *Synthesis*

2.2.1. Synthesis of 4-amino-2-anilinopyridine (aap). Acp (0.500 g, 2.89 mmol) was dissolved in excess aniline (12.3 mL, 101 mmol) in a dried 50 mL round bottom flask equipped with a condenser. The mixture was refluxed overnight under N_2. After the mixture was cooled to room temperature, 20 mL of 10 wt. % NaOH was added to the flask, and the mixture was stirred for 15 min to neutralize the produced HCl. The content was then transferred to a 250 mL round-bottom flask containing 125 mL water. The water and most of the unreacted aniline were removed using a rotovap at 60 °C. The crude product was transferred to a beaker and stirred with hot water, followed by decanting the aqueous phase that contained NaOH, NaCl, or unreacted aniline. The hot water treatment was repeated a few more times until a pale brown solid was formed and later determined to be the aap product. The yield was approximately 83% (0.44 g). The ligand was soluble in isopropanol, methanol, and CH_2Cl_2, but insoluble in water. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the aap solution of methanol : water (9 : 1 v/v) at room temperature. Anal. Calcd for $C_{11}H_{11}N_3$ (%): C, 71.32; H, 5.99; N, 22.69. Found: C, 71.48; H, 6.04; N, 22.68. IR bands (cm^{-1}): 3400m, 3330s, 3140m, 1600s, 1526m, 1442s, 1303sp, 1230w, 974sp, 802s, 747sp, 689sp. ^1H NMR (DMSO-d_6): δ 8.45 (s, 1H), 7.66 (d, 1H, J = 6.0 Hz), 7.57 (dd, 2H, J_1 = 8.0 Hz, J_2 = 1.4 Hz), 7.18 (t, 2H, J = 7.5 Hz), 6.78 (t, 1H J = 7.3 Hz),

6.01 (dd, 1H, J_1 = 5.7 Hz, J_2 = 1.8 Hz), 5.97 (d, 1H, J = 1.8 Hz), 5.71 (s, 2H); ^{13}C NMR (DMSO-d_6): δ 156.8, 155.2, 147.3, 142.6, 128.4, 119.4, 117.8, 103.2, 92.5.

2.2.2. Synthesis of (4,0) $Ru_2(aap)_4Cl$. Aap (1.56 g, 8.44 mmol) was dissolved in 20 mL of isopropanol. To this solution, 0.500 g of $Ru_2(CH_3COO)_4Cl$ (1.05 mmol) was added and the mixture was refluxed overnight under N_2. After cooling to room temperature, the mixture was filtered. The solid was washed with three portions of 20 mL of isopropanol and dried in vacuo. The impure greenish solid was then dissolved in acetone and filtered again. The filtrate was collected and left for evaporation at room temperature. Dark green solid was recovered as the title complex, with 72% (0.74 g) yield. The complex was further purified by silica gel column chromatography using acetone/hexane (7 : 3 v/v) as eluant; only a single green band was observed. Slow evaporation of the complex solution in acetone/toluene media yielded a green crystal suitable for X-ray analysis. The complex was soluble in DMSO and dichloromethane. IR bands (cm^{-1}): 3300w, 1605s, 1480s, 1435sp, 1245sp, 1196sp, 985s, 877s, 696sp.

2.3. *X-ray crystallography*

Single crystals of $C_{11}H_{11}N_3$ were selected and mounted on a Rigaku Saturn724+ (2 × 2 bin mode) diffractometer. The crystal was kept at 295 K during data collection. Using Olex2 [17], the structure was solved with the SHELXS [18] structure solution program using direct methods and refined with the SHELXL [19] refinement package using least squares minimization. Two molecules were seen in the asymmetric unit with one molecule of the two disordered between two positions. The disordered molecules were modeled with restrained distances and thermal parameters.

A green prism of $[2(C_{44}H_{40}ClN_{12}Ru_2)]\cdot 2C_3H_6O\cdot C_7H_8$ having approximate dimensions of 0.20 × 0.12 × 0.10 mm was mounted on a MicroMount. All measurements were made on a Rigaku AFC12/Saturn724 CCD fitted with Mo Kα radiation at −175 ± 2 °C, using the ω scan technique to a maximum 2θ value of 55.0°. Cell constants and an orientation matrix for data collection obtained from a least-squares refinement using 9523 reflections in the range of $4.0° < 2\theta < 80.2°$ corresponded to a primitive triclinic cell. For Z = 1 and FW = 2157.23, the calculated density is 1.503 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be *P-1*. Of the 14,313 reflections that were collected, 8356 were unique (R_{int} = 0.08). The data were corrected for Lorentz and polarization effects.

Structure solution and refinement: The data-set was corrected for absorption based on multiple scans [20] and reduced using standard methods [21]. The structure was solved by direct methods with SHELXS-97 [18] and refined by a full-matrix least-squares procedure on F^2 using SHELXL-97 [19] with anisotropic displacement parameters for non-hydrogen atoms and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + aP^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. All hydrogens were placed on calculated positions, with an isotropic displacement parameter amounting to 1.2–1.5 times the value of the equivalent isotropic displacement parameter of the respective carrier atom. Pertinent crystallographic data for the complex are given in table 1.

Table 1. Crystallographic data and structure refinement for aap and $[2(C_{44}H_{40}ClN_{12}Ru_2)]\cdot 2C_3H_6O\cdot C_7H_8$.

Empirical formula	$C_{11}H_{11}N_3$	$C_{101}H_{100}N_{24}O_2Cl_2Ru_4$
Formula weight	185.23	2157.23
Temperature (K)	295.15	−175 °C
Wavelength (Å)	0.71075	0.71075
Crystal color, shape	White, needle	Green, prism
Crystal dimensions (mm)	0.16 × 0.11 × 0.1	0.20 × 0.12 × 0.10
Crystal system	Monoclinic	Triclinic
Space group	*Cc*	*P-1*
Unit cell dimensions		
a (Å)	5.934(4)	10.652(5)
b (Å)	23.689(15)	12.916(5)
c (Å)	13.716(9)	19.373(8)
α (°)	90	72.97(3)
β (°)	99.146	82.49(3)
γ (°)	90	69.346(19)
V (Å^3)	1904(2)	2383.6(18)
Z	8	1
D_{Calcd} (g cm^{-3})	1.293	1.503
F (0 0 0)	784	1100
μ (Mo Kα, cm^{-1})	0.081	0.742
θ Range for data collection (°)	1.719–25.349	4.7–50.04
Reflections collected/unique	7899/3469 (R_{int} = 0.0662)	14,313/8356 (R_{int} = 0.077)
Max. and min. transmission	0.992 and 0.987	1.000 and 0.514
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3469/285/380	8356/619/0
Goodness-of-fit on F^2	1.008	1.143
Final *R* indices[a]	$[I > 2\sigma(I)]$	$[I > 2\sigma(I)]$
	R_1 = 0.0658, wR_2 = 0.1383	R_1 = 0.066, wR_2 = 0.1603
R indices (all data)	R_1 = 0.1359, wR_2 = 0.1629	R_1 = 0.0750, wR_2 = 0.1647
Largest difference peak and hole (e Å^{-3})	0.128 and −0.135	1.93 and −1.83

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma\, w(F_o^2)^2]^{1/2}$.

3. Results and discussion

3.1. *Synthesis*

The synthetic routes from the starting materials, aniline, and acp, to aap, and finally to $Ru_2(aap)_4Cl$ are outlined in chart 2.

To obtain pure aap, the aniline must be in exceedingly excessive amount. Even at a 10 : 1 aniline-to-acp molar ratio, the resulting products were a mixture of the desired aap and its derivatives that contained various numbers of amino pyridine moieties, as evidenced by the MALDI-MS spectrum [see figure 1(a)]. Under the current experimental conditions, a 35 : 1 aniline-to-acp molar ratio was required to obtain pure aap [figure 1(b)]. Thus, careful control of the aniline-to-acp molar ratio is needed to obtain aap.

Although toluene has been used as a solvent in preparing similar complexes [14], it is not suitable for the present work because neither the aap nor the $Ru_2(CH_3COO)_4Cl$ precursor is soluble in this solvent. As a result, this heterogeneous reaction becomes lengthy and requires high temperature. Moreover, the complex product may not dissolve in toluene; it would be a challenge to separate and purify the final product using chromatographic method. In this work, isopropanol was found to be an ideal solvent, in which both the aap and the precursor could be dissolved, while the complex product would simply precipitate. Therefore, when isopropanol was used as the solvent, the synthesis became a homogeneous reaction, which could be accomplished at lower temperatures and in much shorter time. The

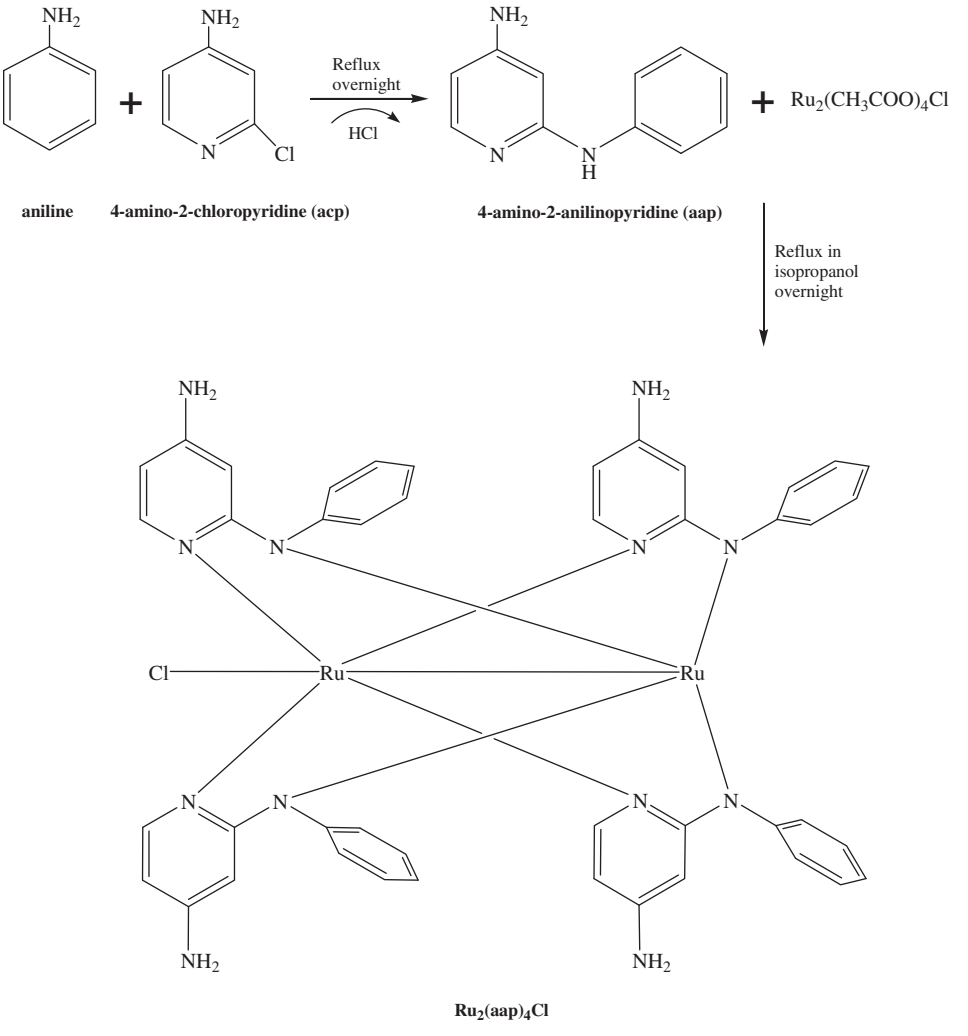

Chart 2. Synthetic routes to aap and $Ru_2(aap)_4Cl$.

diruthenium product could be conveniently collected through filtration. Although four isomers are possible, only the (4,0) isomer was obtained in the present study. Kadish *et al.* reported a diruthenium complex that contained the modified ap ligand involving pyridyl substitution with methyl group at the para position, which yielded a diruthenium complex with (3,1) isomeric form [14].

3.2. *Thermal analysis*

The new aap ligand has a m.p. of 96.0 °C, 3 °C higher than that of acp. But no m.p. of the complex could be detected before it underwent thermal degradation, due to its high molecular mass. Figure 2 exhibits the TGA thermograms of aap and $Ru_2(aap)_4Cl$. Unlike $Ru_2(CH_3COO)_4Cl$, which lost all the ligands in a very narrow temperature range of 310–340 °C (not shown), $Ru_2(aap)_4Cl$ underwent a multiple-step degradation from 258 to

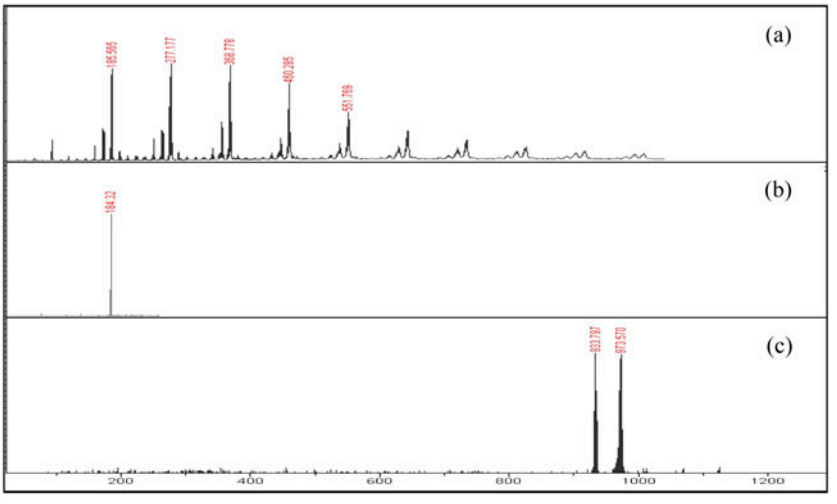

Figure 1. MALDI-MS spectra of products obtained by mixing aniline with acp in molar ratios of (a) 10 : 1, (b) 35 : 1, and (c) $Ru_2(aap)_4Cl$.

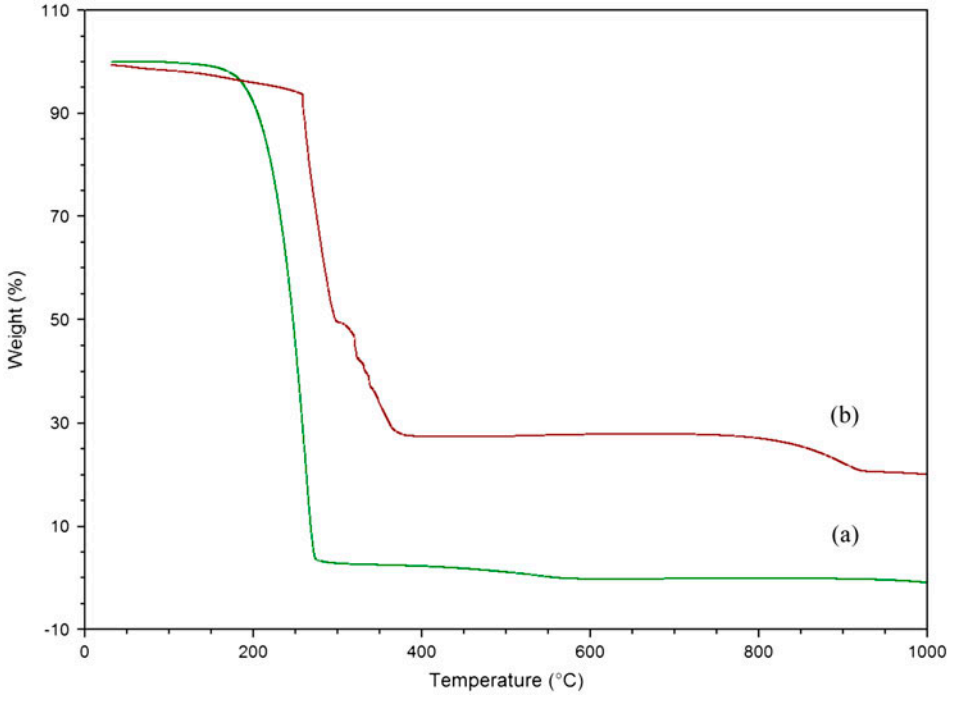

Figure 2. TGA thermograms of (a) aap and (b) $Ru_2(aap)_4Cl$.

366 °C, losing all the ligands except chlorine. Further heating to 1000 °C left the residue of ruthenium metal with a composition of 20.0%, which was in agreement with that calculated (20.7%) for $Ru_2(aap)_4Cl$, proving the successful synthesis of the complex.

3.3. *Spectroscopic characterization*

In order to determine the optimized aniline-to-acp molar ratio for the synthesis of aap, the MALDI-TOF mass spectrometry was employed. When the aniline-to-acp molar ratio was 10 to 1, the reaction between the two starting materials became very complex. As can be seen from figure 1(a), the mass difference between the base peak for aap (*m/z* 184.8 Da) and other peaks was simply an integral multiple of the mass of aminopyridine moiety $[C_5H_3N_2]^+$ (*m/z* 91.5 Da). However, at much higher aniline-to-acp molar ratio (35 : 1), the MALDI spectrum for the reaction system showed only one peak at *m/z* 184.8 Da with little fragmentation [figure 1(b)], indicating the formation of aap ligand. Figure 1(c) presents the mass spectrum of the diruthenium complex $Ru_2(aap)_4Cl$. MALDI analysis yielded two groups of peaks with highest abundance in each group at *m/z* 933.8 and 973.5 Da, respectively. Each group shows a pattern typical of isotopic ruthenium distribution, being similar to other mono- or diruthenium complexes [22]. The two peaks might be attributed to fragments $[M - Cl - 3H_2]^+$ and $[M - H]^+$, respectively, although the assignments looked uncommon. It is the latter mass and the isotopic pattern which provides an important evidence to confirm the 4 : 2 ligand-to-metal molar ratio in the formula.

The aap ligand exhibits several NH stretches in the 3150–3400 cm^{-1} region. Upon coordination to ruthenium, these NH vibrations appear in the same region, suggesting that the NH_2 group on the pyridyl moiety remains uncoordinated. A comparison of the ^1H NMR spectra of aap and the starting materials further reveals the formation of the aap ligand. In general, ^1H NMR frequencies of the aniline moiety in aap shifted downfield relative to pure aniline. In contrary, the proton signals of the pyridine moiety, except the amino protons, shifted upfield after its conjugation with the aniline that is a molecule carrying relatively higher electron density. Replacement of one proton on the NH_2 group of aniline by pyridine resulted in the largest downfield shift of the NH proton from 4.99 to 8.55 ppm, indicating that the electron density on nitrogen was largely shared by the pyridine. However, no systematic shifts were observed in their ^{13}C NMR spectra. Carbons attached to the amino groups in the aniline and pyridine, respectively, shifted in opposite directions, one from 148.6 to 142.6 ppm and the other from 150.8 to 155.2 ppm, further substantiating the mutual influence due to the formation of a larger conjugated π system.

3.4. *X-ray analysis*

The stoichiometry of the diruthenium complex was also supported by single-crystal X-ray diffraction. ORTEP diagrams of aap and $Ru_2(aap)_4Cl$ with the atom numbering are shown in figure 3(a) and (b), respectively. Selected bond lengths, bond angles, and torsion angles for aap and $Ru_2(aap)_4Cl$ are summarized in table 2. Similar to other diruthenium complexes, the geometries around Ru1 and Ru2 were octahedral and square pyramidal, respectively. As revealed by the structure, the diruthenium complex is a (4,0) isomer, where Ru1 is coordinated with four pyridyl nitrogens (N_p) and one chloride, and Ru2 is coordinated with four aniline nitrogens (N_a). The Ru–Ru bond length is 2.2901(13) Å, which is almost the same as reported for similar diruthenium complexes with other substituted-ap ligands [23, 24]. The Ru–Cl bond distance is 2.4947(19) Å, comparable to that in the methyl-substituted complex (2.4770(13) Å) [14]. All these values agree well with previously reported diruthenium complexes with four identical substituted-ap bridging ligands [10].

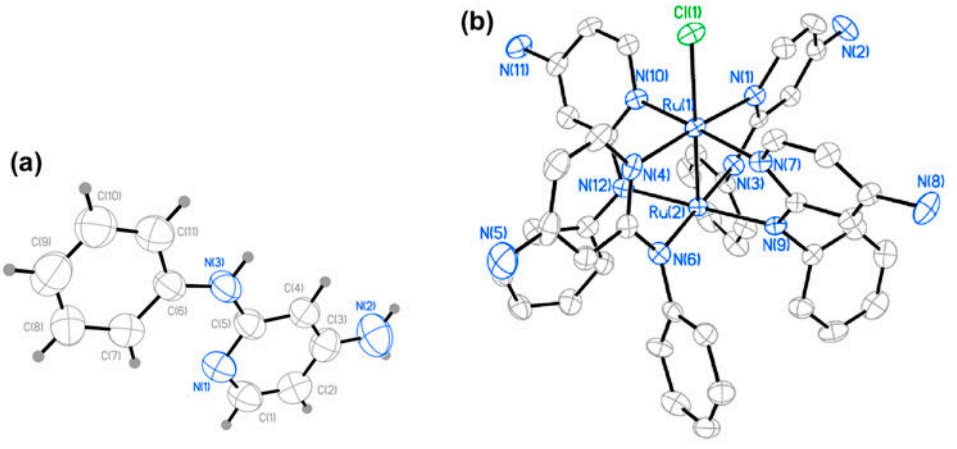

Figure 3. ORTEP representations of (a) aap and (b) $Ru_2(aap)_4Cl$ (H atoms omitted for clarity). Ellipsoids are at 50% probability.

Table 2. Selected bond lengths, bond angles, and torsion angles for aap and $Ru_2(aap)_4Cl$.

	$Ru_2(aap)_4Cl$	aap
Bond lengths (Å)		
Ru1–Ru2	2.2901(13)	
Ru1–Cl1	2.4947(19)	
Ru1–N7	2.092(5)	
Ru1–N1	2.097(5)	
Ru1–N10	2.113(5)	
Ru1–N4	2.118(5)	
Ru2–N3	2.045(5)	
Ru2–N9	2.049(5)	
Ru2–N6	2.052(5)	
Ru2–N12	2.062(5)	
N1–C5	1.385(7)	1.31(2)
N3–C5	1.332(8)	1.42(3)
N3–C6	1.437(8)	1.41(3)
Bond angles (°)		
Ru2–Ru1–Cl	179.39(3)	
N1–Ru1–N7	91.1(2)	
N1–Ru1–N10	86.5(2)	
N1–Ru1–N4	176.4(2)	
N7–Ru1–N4	88.0(2)	
N1–Ru1–Ru2	88.17(14)	
C1–N1–C5	117.4(5)	112.7(18)
N1–C5–N3	116.5(5)	117.2(2)
C5–N3–C6	119.8(5)	128.8(15)
Torsion angles (°)		
Cl1–Ru1–Ru2–N3	62(4)	
N1–Ru1–Ru2–N3	−17.4(2)	
N7–Ru1–Ru2–N3	108.5(2)	
N1–C5–N3–C6	164.4(6)	2.7(8)

Upon complexation, the bond lengths involving pyridyl nitrogen N1–C1 and N1–C5 of aap were lengthened (see table 2). However, the bond lengths involving the aniline nitrogen N3–C5 and N3–C6 were shortened. As a result, the bond angle of C1–N1–C5 of the pyridyl group increased from 112.7(18)° to 117.4(5)°, while the bond angle of C5–N3–C6 of the aniline moiety decreased from 128.8(18)° to 119.8(5)°. Concomitant changes in bond lengths and angles are due to formation of the five-member chelate ring. The bond angle of Ru2–Ru1–Cl [179.39(4)°] is closer to linear than that in the methyl-substituted complex (177.64(4)°) [14]. Other bond angles, such as N_p–Ru1–Cl, Ru2–Ru1–N_p or Ru2–Ru1–N_a, are in agreement with the expected geometry around Ru1 and Ru2, respectively. It seems that the stronger electron-donating power of the amino group on the pyridine results in adoption of a (4,0) configuration rather than the (3,1) fashion. Intermolecular hydrogen bonds are also observed in the crystal structure. Although the hydrogen bond between N11–H and Cl1 (aminopyridyl, H···Cl, 2.76 Å; N–H···Cl 157°) is rather weak, it is this hydrogen bond that causes the two diruthenium complexes to interact in a head-on fashion, i.e. their chloro ligands pointing to each other (see figure 4). The solvated acetone molecules then bring the two diruthenium complexes together through the formation of stronger hydrogen bonds between N8–H and O1 (aminopyridyl, H···O, 2.34 Å; N–H···O 140°) and between N2–H and O1′ (aminopyridyl, H···O, 2.45 Å; N–H···O 137°). The uncoordinated aap is basically planar (torsional angle 2.7°). However, when aap is coordinated to ruthenium, the ligand becomes twisted by approximately 15° from planarity (torsional angle 165°).

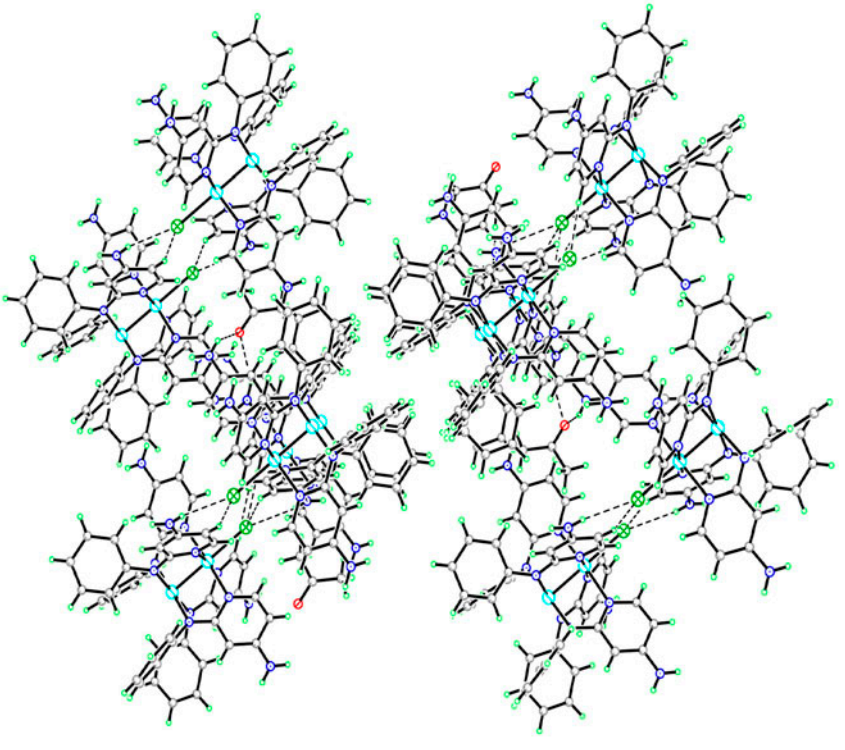

Figure 4. Packing diagram of the $Ru_2(aap)_4Cl$ complex, viewed down the *a*-axis.

4. Conclusion

In this paper, we present the synthesis and characterization of a new bridging ligand, 4-amino-2-anilinopyridine (aap) and its diruthenium complex (4,0) $Ru_2(aap)_4Cl$. The aap was obtained by refluxing a mixture of aniline/4-amino-2-chloropyridine with a 35 : 1 molar ratio. The (4,0) $Ru_2(aap)_4Cl$ was prepared in isopropanol by reacting aap with $Ru_2(CH_3COO)_4Cl$ (8 : 1 molar ratio) under N_2. Both compounds were characterized by thermal analysis, MALDI-TOF mass spectrometry, IR and NMR (^1H and ^{13}C) spectroscopy, and X-ray crystallography. The structural analysis revealed that the complex exists as a (4,0) isomer, in which the amino group on the pyridyl moiety was not involved in chemical bonding.

Supplementary material

Crystallographic data for the aap ligand and its diruthenium complex have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 965916 and 965917, respectively. Copies of the data can be obtained, free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223/336 033 or E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We would like to thank Dr. Tuan D. Phan for his participation in discussions at the early stage of this research. We are grateful to Dr. Lee M. Daniels (Rigaku Americas Corp., 9009 New Trails Drive, The Woodlands, Texas, USA) for taking the initial X-ray structure data for the aap ligand and Dr. Joseph H. Reibenspies (Department of Chemistry, X-ray Diffraction Laboratory, Texas A&M University, College Station, Texas, USA) for refining the data. X.W. would like to acknowledge the grant funding support from NSF-CREST Program. N.V.N. is grateful to the Title III fellowship program from Texas Southern University for financial assistance.

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