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SYNTHESIS OF 2-CHLORO-8-(2-PYRIDYL)-1-AZAAZULENE AND ITS METAL COMPLEXES

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Abstract - Reaction of 2-chloro-1-azaazulenes with 2-pyridyllithium followed by dehydrogenation by chloranil gave 8-(2-pyridyl) -1-azaazulene (**2**). Formation of metal complexes (M = Cu, Fe, Pd) of **2** was achieved. The reaction of **2** with Cu(I) gave 1:1-complex (**3**) and 2:1-complex (**4**). Complex (**3**) was deduced to have a polymeric chain structure with the copper center is +1. The ESR spectrum study of **4** showed that the copper center is +2. The structure of **4** was decided by X-Ray structural analysis and it is shown that the complex takes a trigonal bi-pyramidal structure.

INTRODUCTION

The chemistry of azaazulenes, being non-alternant concjugated heterocycles, is of interest for their physical and chemical properties as well as physiological properties.[1] Although it is expected that non-alternant bidentate ligand would allow production of coordination molecules showing an interesting interaction between the ligand and the central metal, such researches were few. Recently, we reported the formation and structural studies of the complexes of 8-methylamino-1-azaazulene with boron atom[2] and 8-amino-1-azazulene with phosphorous atom.[3] In these systems, N-B-N and N-P-N interactions were observed and new ring system formation was achieved. For the extension of azaazulene chemistry[1] and construction of novel non-alternant bidentate ligands and their metal complexes, we examined the synthesis and complexation of 8-(2-pyridyl)-1-azaazulene derivatives.

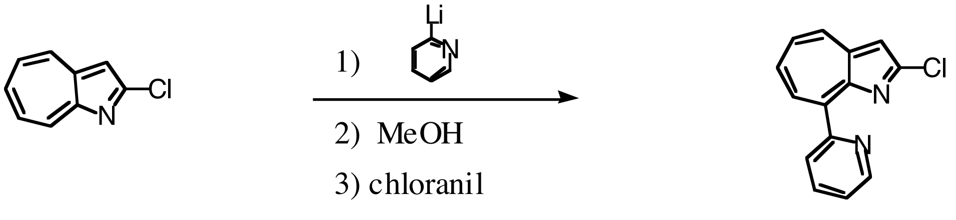
RESULTS AND DISCUSSION

It is known that reaction of alkyllithium reagents mainly added to 8-position on 1-azaazulene nuclei,[4-8] and this time we examined the generation and reaction of 2-pyridyllithium with 1-azaazulene. Thus, treatment of 2-bromopyridine with butyllithium at –90 ℃ and successive reaction of 2-chloro-1-azaazulene (**1**) followed by the dehydrogenation with tetrachloro-*o*-benzoquinone (*o*-chloranil) gave 2-chloro-8-pyridyl-1-azaazulene (**2**) in 73% together with recovered **1** (20%). ^{1}H NMR spectra of **2** in some variety of solvents are shown in Table 1. In the polar solvents, the signals sifted to low field, especially at H-4 and H-H-6, and an extra large down field shift was seen in CF_3CO_2D (TFA-*d*). The results suggest that compound (**2**) has a polar character and a protonation easily occurred at ring nitrogen. Therefore, it is expected that complexation of **2** with metal would easily occur.

Table 1. ^{1}H NMR spectra of **2** (chemical shifts: δ in Hz).

Solvent	H-3	H-4	H-5	H-6	H-7	H-3’	H-4’	H-5’	H-6’
$CDCl_3$	7.32	8.49	7.69	7.98	8.34	8.31	7.88	7.40	8.81
CD_3CN	7.41	8.65	7.81	8.09	8.24	8.10	7.91	7.47	8.78
MeOD	7.46	8.73	7.88	8.01	8.13	8.12	7.96	7.56	8.74
DMSO-d_6	7.58	8.77	7.99	8.19	8.27	8.15	7.99	7.54	8.80
TFA-*d*	7.81	9.37	8.75	8.87	8.69	8.65	9.02	8.46	9.24

Because Cu(I) complexes with polydentate nitrogen ligands heve received attention[9] within the fields of supramolecular chemistry [10] and bioinorganic chemistry,[11] we examined the complexation of **2** with copper at first. Thus, treament of **2** with an equivalent molar of $[Cu(MeCN)_4]PF_6$ in dry dichloromethane for 5 h at room temperature gave **3** in 83%yield. Compound (**3**) was analyzed as 1:1-complex by elemental analysis and ICP-AES analysis. The ^{1}H NMR spectrum of **3** showed some broadening signals at δ 7.3



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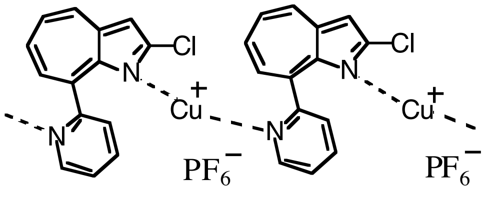

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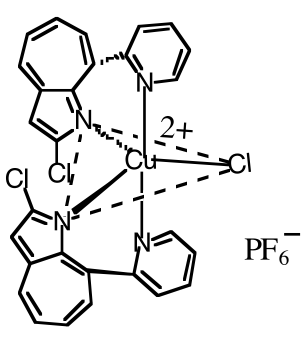

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– 8.8 and we could not assign the structure clearly. In its FABMS spectrum, peaks of rather high molecular weight were seen, and peaks at *m/z* 629, 627, and 625 were assigned as ($C_{14}H_9N_2Cl$-Cu-$C_{14}H_9N_2Cl$-Cu). Although the distinct molecular weight and structure could not be decided, it is considered that **3** had a polymeric chain structure. The inter distance of N-1—N-1' on **2** is calculated as 2.687 Å by the molecular orbital calculation using MM2. It is considered that two-coordinate Cu(I) ion prefer to take linear form. Therefore, on the complexation of **2** with Cu(I) ion, the Cu(I) ion takes inter-moleculer coordination between discrete molecules rather than chelation mode between N-1 and N-1', where short distance would constrain the bending of N-1—Cu—N-1'.

When **2** was treated with one-third equivalent molar of $[Cu(MeCN)_4]PF_6$, **4** was obtained in 81%yield. Compound (**4**) was analyzed as 2:1-complex and takes one chloride as a ligand on the basis of elemental analysis and ICP-AES analysis. The ^{1}H NMR spectrum of **4** could not give sufficient figure except for some broad signals, but simple ESR spectrum was obtained ($g_{\perp}$ = 2.068, $g_{//}$ = 2.279, $A_{//}$ = 15.14 mT in DMF) (Figure 1). The oxidation state of the copper center in the complex (**4**) is +2; this shows that in the reaction Cu(I) was oxidized to Cu(II). In the spectrum, fine structure was not seen and the signals appeared at ordinal field as Cu(II), therefore it considered that the charge did not delocalize to the azaazulene ring.

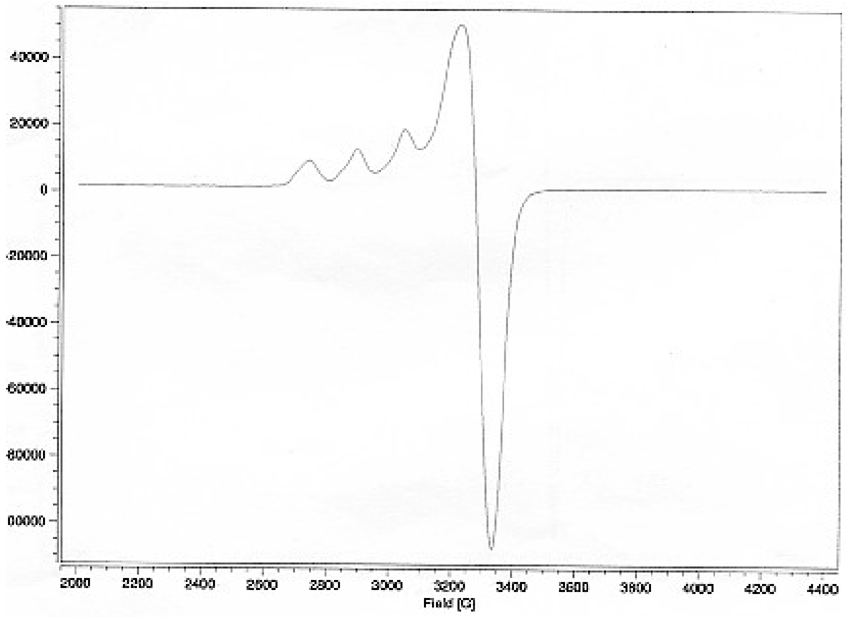


Figure 1. ESR spectrum of **4** in DMF.

The structure of **4** is decided by X-Ray structure analysis (Figure 2).[12] Interestingly, the center copper coordinates to four nitrogen atoms and a chloride (penta-coordinate) and takes a trigonal bi-pyramidal structure. The bond angle of N(2)—Cu(1)—N(4) is 170.1(3)° and it is considered that two pyridine rings occupy apical position. Although the bond length of Cu—Cl is 2.287(3) Å is rather short, it is reasonable to assign the bond as equatorial from the comparison with the bond lengths of $CuCl_6$; Cu—Cl (eq) =

2.263(6) Å and Cu—Cl (ap) = 2.991(6) Å.[13] Chloride anion would be produced by the decomposition of dichlromethane or chloroform used as the solvent.

It is considered that Fe(II) or Pd(II) could take hexa-coordinate or tetra-coordinate form and it is expected that the complexes form chelation mode. Therefore we examined the formation of complex of **2** with $FeCl_2$ next, expecting the formation of **5**. Thus **2** was treated with $FeCl_2 \cdot 4H_2O$ in dry acetonitrile for 5 h at room temperature, and reddish brown powder (**6**) was obtained in 77% along with recovered **2** (14%).

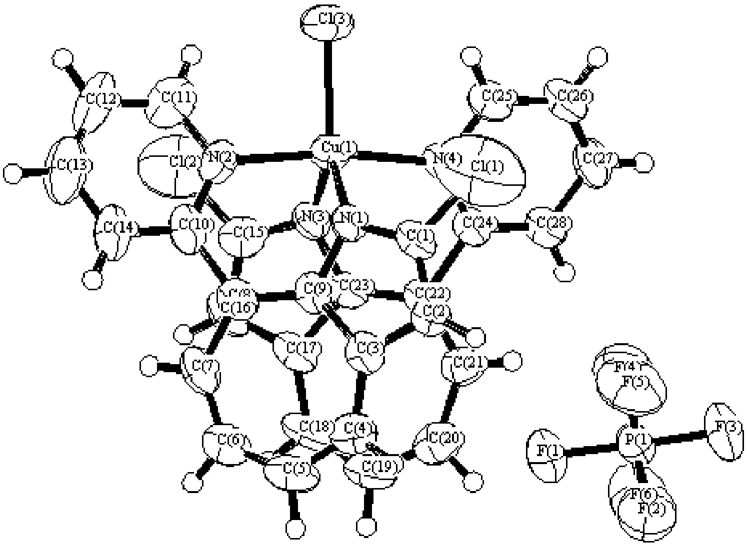
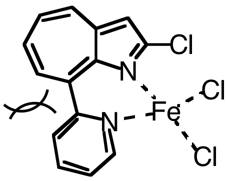


Figure 2. ORTEP drawing of **4** with thermal ellipsoids (50% probability).
Selective bond lengths (Å): Cu(1)—Cl(3) 2.287(3), Cu(1)—N(1) 2.043(8), Cu(1)—N(2) 2.028(9), Cu(1)—N(3) 2.191(7), Cu(1)—N(4) 2.191(7), C(4)—C(5) 1.37(1), C(5)—C(6) 1.36(1), C(6)—C(7) 1.37(1), C(7)—C(8) 1.43(1), C(8)—C(9) 1.38(1),
Selective bond Angles (°): Cl(3)—Cu(1)—N(1) 138.2(2), Cl(3)—Cu(1)—N(2) 96.3(3), Cl(3)—Cu(1)—N(3) 111.5(2), Cl(3)—Cu(1)—N(4) 93.2(2), N(1)—Cu(1)—N(2) 84.2(3), N(1)—Cu(1)—N(3) 110.3(3), N(1)—Cu(1)—N(4) 90.3(3), N(2)—Cu(1)—N(3) 91.3(3), N(2)—Cu(1)—N(4) 170.1(3), N(3)—Cu(1)—N(4) 82.3(3).

Although the compound (**6**) was analyzed as 1:1-complex by elemental analysis and ICP-AES analysis, its FABMS spectrum showed the peaks of rather high molecular weight; peaks at *m/z* 575, 573, and 571were assigned as ($C_{14}H_9N_2Cl$-FeCl-$C_{14}H_9N_2Cl$). Therefore, the structure of **6** is feasible as a polymeric chain structure, where the central Fe(II) ion would takes a tetrahedral mode. Steric hindrance of 8-(2pyridyl)-1-azaazulene would constrain the structure, and the pyridine ring would twist against the plane of the 1-azaazulene ring. The reaction of **2** with Fe(II) is slow and the yield of the complex was low in comparison with Cu(I): the result suggest that the **2** has possibility to discriminate metals.



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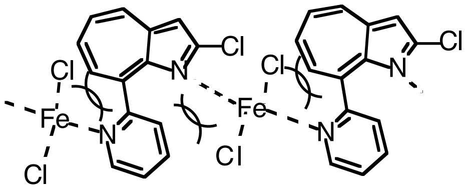

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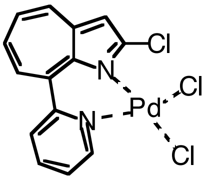
Expecting the formation of **7** or **8**, since Pd(II) would prefer to have a coordination of square plane mode or of octahedral mode, we next examined the reaction of $PdCl_2(PhCN)_2$ and **2**. Thus treatment of $PdCl_2(PhCN)_2$ **2** in dry benzene for 1 h at room temperature gave a red powder. In spite of the difference of the ratio of the reagents, the product was same, in contrast with the case of **2** with Cu(I). The compound was analyzed as 1:1-complex by elemental analysis and ICP-AES analysis, and its FABMS spectrum showed the peaks of rather high molecular weight. From the results, the powder was deduced as for polymer (**9**). The ^{1}H NMR spectrum of **9** in DMSO-d_6 showed rather complex feature and it seems that five Pd—pyridyl-1-azaazulene moieties ($C_{14}H_9N_2Cl_3Pd$ × 5) take one group; this would supports that **9** has a polymeric structure and the central Pd(II) ion would take a tetrahedral mode. When the spectrum was taken in TFA-*d*, it showed the same figure with that of **2**.



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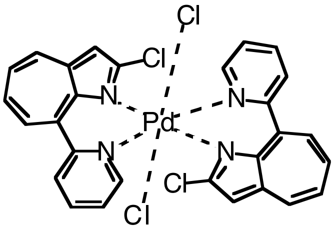

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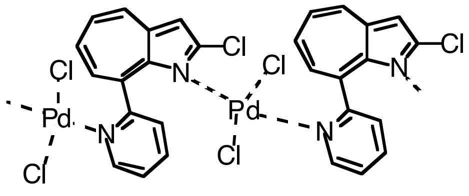

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CONCLUSION

Formation of metal complexes of 8-(2-pyridyl)-1-azaazulene system with Cu(I), Cu(II), Fe(II), and Pd (II) was achieved. Treatment of 8-(2-pyridyl)-1-azaazulene with Cu(I) gave 1:1-complex (**3**), having a polymeric chain structure, or 2:1-complex (**4**), having a trigonal bipiramidal structure where the oxidation state of the copper center in the complex (**4**) is +2, depending upon reagent ratio.

EXPERIMENTAL

Mps are measured using a Yanagimoto micro-melting apparatus and uncorrected. ^{1}H NMR spectra were recorded on a Bruker AVANCE 400S (400 MHz) using deuteriochloroform as a solvent with tetramethylsilane as an internal standard unless otherwise stated; *J* values are recorded in Hz. ESR spectra were recorded on a Elexsys E500 Spectrometer. IR spectra were recorded for KBr pellets on a Nicolet FT-IR Impact 410. MS spectra were taken with on an LC-MS Waters Integrity System and FAB MS were taken with JEOL JMS-01SG-2 spectrometer. Elemental analyses were taken with a Perkin Elmer 2400II, and ICP-AES were taken with Varian ICP-AES Liberty. Kieselgel 60 was used for column chromatography and Kieselgel 60G was used for thin-layer chromatography.

Synthesis of 2-chloro-8-(2-pyridyl)-1-azaazulene (2)

Under argon atmosphere, 1.5 M butyllithium (2.6 mL, 3.90 mmol) was added to the solution of 2-bromopyridine (0.30 mL, 3.0 mmol) in dry ether (20 mL) at –90 ℃. To the mixture 2-chloro-1-azaazulene (**1**) (0.492 g, 3.00 mmol) in dry ether (20 mL) was added, and the mixture was stirred for 1.5 h at –30 ℃, then methanol (5 mL) was added. After the mixture was warm to rt, *o*-chloranil (0.738 g, 3.0 mmol)was added to the mixture and the mixture was stirred for 17 h. To the mixture was added water, and the mixture was extracted with chloroform, dried over sodium sulfate, and evaporated. The residue was chromatographed on silica gel column with ethyl acetate—hexane (1 : 5) to give 2-chloro-8-(2-pyridyl)-1-azaazulene (**2**) (0.526 g, 73%) and recovered (**1**) (0.097 g, 20%).

2: Orange needles (from hexane-dichloromethane), mp 137—139 ℃; δ_H 7.32 (1H, s), 7.40 (1H, ddd, *J* 7.6, 4.8, and 1.2), 7.69 (1H, dd, *J* 9.8 and 9.4), 7.88 (1H, ddd, *J* 7.8, 7.6 and 1.8), 7.98 (1H, ddd, *J* 11.6, 9.8 and 1.1), 8.31 (1H, dddd, *J* 7.8, 1.2, 1.1, and 0.9), 8.34 (1H, d, J 11.6), 8.49 (1H, dm, *J* 9.4), and 8.81 (1H, ddd, *J* 4.8, 1.7, and 0.9); *m/z* (rel intensity) 242 (M+, 36), 241 (65), 240 (M+, 92), 239 (100), 205 (50), 177 (12), 120 (11), 102 (9), and 89 (15). *Anal.* Calcd for $C_{14}H_9N_2Cl$: C, 69.86; H, 3.77; N, 11.64. Found: C, 69.99; H, 3.58; N, 11.45.

Synthesis of Cu-complex with 2

A) – A mixture of $[Cu(MeCN)_4]PF_6$ (0.141 g, 0.38 mmol)and **2** (0.0912 g, 0.38 mmol) in dry dicchloromethane (5 mL) was stirred for 5 h at rt, and the filtration of the precipitates gave **3** (0.142g, 83%) as reddish brown powder.

3: Red brown powders (from methanol-dchloromethane), mp 235—239 ℃; FABMS, *m/z* (rel intensity) 755 (0.6), 753 (0.9), 751 (0.6), 711 (1.0), 709 (1.2), 707 (0.8), 648 (0.8), 646 (1.2), 644 (1.0), 629 (7), 627 (13), 625 (9), 547 (4), 545 (10), 543 (9), 387 (6), 385 (7), 307 (16), 306 (15), 305 (77), 303 (100), 216 (17), and 205 (12). *Anal.* Calcd for $C_{14}H_9N_2ClCuF_6P\cdot 0.5CH_2Cl_2$: C, 35.42; H, 2.05; N, 5.70; Cu, 12.93. Found: C, 35.37; H, 2.20; N, 5.36. ICP-AES; Cu, 13.32.

B) - A mixture of $[Cu(MeCN)_4]PF_6$ (0.0133 g, 0.035 mmol) and **2** (0.025 g, 0.104 mmol) in dry dichloromethane (5 mL) was stirred for 5 h at rt, Then hexane (1 mL) was added to the mixture and **4** (0.0155 g, 81%) was collected by the filtration.

4: Red prisms (from methanol-chloroform), mp 210—215 ℃; FAB MS, *m/z* (rel intensity) 547 (15), 545 (37), and 543 (M^+, 35), 526 (6), 524 (8), 510 (5), 508 (10), 491 (16), 489 (31), 307 (15), 305 (70), 303 (91), 251 (25), 243 (16), 241 (46), 237 (100), 205 (19). *Anal.* Calcd for $C_{28}H_{18}N_4Cl_3CuF_6P$: C, 46.37; H, 2.50; N, 7.72; Cu, 8.76. Found: C, 46.22; H, 2.46; N, 7.89. ICP-AES; Cu, 8.51.

Synthesis of Fe-complex with 2

A mixture of $FeCl_2\cdot 4H_2O$ (0.075 g, 0.38 mmol) and **2** (0.091 g, 0.38 mmol) in dry acetonitrile (5 mL) was stirred for 5 h at rt, and the filtration and washed with water and chloroform of the precipitates gave **6** (0.108g, 77%) as reddish brown powder. From the filtrate, **2** was recovered (0.013 g, 14%).

6: Red brown powders (from methanol-chloroform), mp 275—278 ℃ (decomp); FABMS, *m/z* (rel intensity) 575 (0.5), 573 (1.3), 571 (1.3), 335 (1.5), 333 (8), 331 (12), 243 (35), 242 (21), 241 (100), 239 (4), 237 (16), 207 (7), and 205 (10). *Anal.* Calcd for $C_{14}H_9N_2Cl_3Fe\cdot 0.5CHCl_3$: C, 44.46; H, 2.45; N, 7.15; Fe, 14.26. Found: C, 44.92; H, 2.49; N, 6.64. ICP-AES; Fe, 14.85.

Synthesis of Pd-complex with 2

A mixture of $PdCl_2(PhCN)_2$ (0.146 g, 0.38 mmol) and **2** (0.091 g, 0.38 mmol) in dry benzene (5 mL) was stirred for 1 h at rt, and the filtration of the precipitates gave **9** (0.158g, 99.5%) as red powder.

9: Red brown powders, mp 235—240 ℃ (decomp) ; δ_H (DMSO-d_6) 6.73 (1H, s), 7.18 (1H, s), 7.34 (1H, like-t, *J* 9.7), 7.55 (1H, like-t, *J* 5.2), 7.57 (2H, s), 7.8-7.9 (6H, m), 7.91 (1H, like-t, *J* 9.8), 7.98 (1H, like-t, *J* 8.0), 7.99 (2H, like-t, *J* 7.7), 8.1-8.3 (10H, m), 8.41 (1H, t, *J* 9.8), 8.47 (1H, d, *J* 5.8), 8.49 (1H, d, *J* 9.7), 8.57 (1H, d, *J* 10.7), 8.60 (2H, t, *J* 10.0), 8.71 (1H, d, *J* 10.6), 8.77 (2H, d, *J* 9.9), 8.80 (2H, d, *J* 4.9), 8.95 (2H, d, *J* 10.6), 9.03, (2H, d, *J* 9.6), 9.18 (2H, d, *J* 5.1), 9.33 (1H, d, *J* 4.7), and 9.58 (1H, d, *J* 5.1); δ_H (TFA-d_4) 7.81 (1H, s), 8.46 (1H, dd, *J* 7.6 and 5.3), 8.63 (1H, dd, *J* 7.9), 8.68 (1H, d, *J* 10.3), 8.75 (1H, dd, *J* 9.8 and 9.7), 8.86 (*1*H, dd, *J* 10.3 and 9.7), 9.02 (*1*H, dd, *J* 7.9 and 7.6), 9.24 (1H, br d, *J* 5.3) and 9.37 (1H, d, *J* 9.7); FABMS, *m/z* (rel intensity) 623 (1.6), 621 (2.8), 385 (9), 383 (14), 381 (12), 348 (35), 346 (36), 243 (64), 242 (81), and 241 (100). *Anal.* Calcd for $C_{14}H_9N_2Cl_3Pd\cdot 1/2C_6H_6$: C, 44.67; H, 2.65; N, 6.13; Pd, 23.38. Found: C, 44.33; H, 2.56; N, 5.64. ICP-AES; Pd, 23.29.

X-Ray structure determination

Crystal data of 4: Red prism, $C_{28}H_{18}N_4Cl_3CuF_6P$, *M*=725.35, triclinic, space group P1, *a*=11.287(5), *b*=16.250(6), *c*=8.008(2) Å, α=99.40(3)°, β=99.48(3)°, γ=88.83(3)°, *Z*=2, *V*=1443.5(9) Å^3, D_{calcd}=1.669 g/cm^3, crystal dimensions 0.14 x 0.68 x 1.00 mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-Kα radiation. Total 5372 reflections (unique 5088) were collected using ω–2θ scan technique with in a 2θ range of 50.0°. The structure was solved by direct methods (SIR92),[14] and refined by a full-matrix least-squares method using TEXAN structure analysis software[15] with 388 variables and 3218 observations observed reflections [$I > 2\sigma(I)$]. The weighting scheme $\omega = 4Fo^2/\sigma^2(Fo^2)$ gave satisfactory agreement analyses. The final refinement converged to $R = 0.086$ and $Rw = 0.087$.

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