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Synthesis and X-Ray Crystal Structure of the Dicopper(I) Complex of 2-(Diphenylphosphino)pyridine (Ph_2Ppy). $[Cu_2(\mu\text{-}Ph_2Ppy)_2(CH_3CN)_2](PF_6)_2$

Masahiko Maekawa, Megumu Munakata,*,† Susumu Kitagawa,†
and Teijiro Yonezawa
Research Institute for Science and Technology, Kinki University, Kowakae, Higashi-Osaka 577
† Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka 577

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Synopsis. The dicopper(I) complex with 2-(diphenylphosphino)pyridine (Ph_2Ppy), $[Cu_2(\mu\text{-}Ph_2Ppy)_2(CH_3CN)_2](PF_6)_2$ has been prepared. The crystal structure has been determined crystallographically: Space group $P\bar{1}$, a=10.807(6), b=11.756(8), c=8.606(7) Å, α=90.36(6), β=95.98(5), γ=92.90(5)°, Z=1, R=0.067. The two copper atoms are bridged by two Ph_2Ppy molecules in a head-to-tail arrangement, resulting in a rare staggered conformation of the eight-membered ring $Cu_2P_2N_2C_2$, whose factor is concerned with the coordination numbers of the central metal atoms. ^1H NMR studies show that the ligand of a CH_3CN in the titled compound undergoes dissociation in acetone solution.

2-(diphenylphosphino)pyridine (Ph_2Ppy) can form dimetal complexes[1–4] having an eight-membered ring $M_2P_2N_2C_2$, because of its ability to act as a bidentate bridging ligand. The two sort donor atoms in Ph_2Ppy stabilize metals in the lower oxidation state. However, there is sparse literature on its copper(I) and silver(I) complexes. Recently the dicopper(I) complex containing three Ph_2Ppy molecules as bridging ligands was reported.[5] The framework of the eight-membered ring gives an eclipsed[1–4,6–11] and a staggered conformation.[12] The latter seldom occurs in metal complxes, whereas the former often occurs in various metal complexes.

We have synthesized the dicopper(I) complex bridged by two Ph_2Ppy molecules which form a eight-membered ring and have determined the crystal structure in order to clarify the factors governing the eclipsed and staggered conformations.

Table 1. Crystal Data for $[Cu_2(\mu\text{-}Ph_2Ppy)_2(CH_3CN)_2](PF_6)_2$

Formula	$Cu_2C_{38}N_4H_{34}P_2F_{12}$
Formula weight	1025.68
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell constants	
a/Å	10.807(6)
b/Å	11.756(8)
c/Å	8.606(7)
α/°	90.36(6)
β/°	95.98(5)
γ/°	82.90(5)
V/Å^3	1079.1
Z	1
Density/g cm^{-3}	3.935
Crystal size/mm	0.3×0.3×0.3
Radiation	Mo $K\alpha$
λ (Mo $K\alpha$)/Å	0.71073
μ (Mo $K\alpha$)/cm^{-1}	11.42
Scan mode	ω–2θ
Scan rate/° min^{-1}	8
Scan range/°	$1.4194+0.5\tan\theta$
2θ range/°	2—60
Number of observed reflections	5354
Reflections used in refiment	3753 ($F_o>3\sigma(F_o)$)
F(000)	486
R	0.067
R_w	0.067

$R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$. $R_w=\{\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$, where $w=1/\sigma^2(F_o)$.

Experimental

Preparation of $[Cu_2(\mu\text{-}Ph_2Ppy)_2(CH_3CN)_2](PF_6)_2$. All operations were carried out under an atmosphere of purified argon. The reaction of Ph_2Ppy[13] (52.7 mg, 0.2 mmol) with $[Cu(CH_3CN)_4]PF_6$[14] (74.5 mg, 0.2 mmol) in dry methanol (10 ml) gave a clear solution, which was allowed to stand for

Table 2. Atomic Parameters for Non-Hydrogen Atoms in $[Cu_2(\mu\text{-}Ph_2Ppy)_2(CH_3CN)_2](PF_6)_2$

Atom	x	y	z	B_{eq}
Cu	−0.1030(1)	−0.1074(1)	0.0106(1)	4.28(4)
P(1)	−0.1512(1)	0.0659(1)	0.1031(2)	3.55(6)
P(2)	−0.3141(2)	−0.4507(2)	0.3033(2)	5.6(1)
F(1)	−0.4300(6)	−0.4220(8)	0.1924(9)	17.4(6)
F(2)	−0.2668(7)	−0.5346(5)	0.1740(7)	12.7(4)
F(3)	−0.2472(7)	−0.3589(5)	0.2343(7)	12.2(4)
F(4)	−0.3580(7)	−0.3675(6)	0.4295(8)	13.9(5)
F(5)	−0.3734(10)	−0.5432(7)	0.3753(9)	19.9(8)
F(6)	−0.1929(7)	−0.4822(8)	0.4110(9)	16.9(6)
N(1)	0.0617(4)	−0.2023(4)	−0.9091(5)	3.9(2)
N(2)	−0.2150(5)	−0.2145(4)	−0.0714(6)	4.6(2)
C(1)	0.0624(6)	−0.2802(5)	0.2046(8)	5.1(3)
C(2)	0.1734(7)	−0.3333(6)	0.2782(9)	6.2(3)
C(3)	0.2839(6)	−0.3101(6)	0.2335(8)	5.9(3)
C(4)	0.2845(6)	−0.2324(5)	0.1123(8)	4.7(2)
C(5)	0.1700(5)	−0.1797(4)	0.0453(6)	3.7(2)
C(11)	−0.0325(5)	0.1160(5)	0.2443(6)	3.7(2)
C(12)	0.0572(5)	0.0345(5)	0.3210(7)	4.0(2)
C(13)	0.1449(6)	0.0694(6)	0.4342(7)	5.1(3)
C(14)	0.1446(6)	0.1818(6)	0.4725(7)	5.4(3)
C(15)	0.0566(6)	0.2638(6)	0.3978(8)	5.4(3)
C(16)	−0.0327(6)	0.2303(5)	0.2836(7)	4.6(2)
C(21)	−0.2960(5)	0.0828(5)	0.1966(7)	4.0(2)
C(22)	−0.3713(6)	−0.0022(7)	0.1808(9)	6.1(3)
C(23)	−0.4800(8)	0.0058(9)	0.2530(11)	7.9(5)
C(24)	−0.5108(6)	0.0964(8)	0.3432(9)	6.9(4)
C(25)	−0.4362(6)	0.1808(7)	0.3638(9)	6.3(4)
C(26)	−0.3289(6)	0.1742(6)	0.2897(9)	5.7(3)
C(31)	−0.2687(6)	−0.2873(5)	−0.1107(8)	4.9(3)
C(32)	−0.3380(9)	−0.3816(6)	0.8376(11)	8.1(5)

$B_{eq}=(4/3)\{\Sigma_i\Sigma_{ij}B_{ij}\boldsymbol{a}_i\boldsymbol{a}_j\}$.

two days at 0 °C. A small colorless crystal, $[Cu_2(\mu\text{-}Ph_2Ppy)_2(CH_3CN)_2](PF_6)_2$ (**1a**) was obtained together with many pale yellow-green crystals (**1b**).[15] The structure of **1a** was determined by X-ray crystallography, but that of **1b** could not determined because of the decay of the reflection intensities during data collection of the X-ray diffraction. ^1H NMR ($(CD_3)_2CO$) **1a** δ=9.45 (d, 6-H), 8.16 (t, 4-H), 7.93 (t, 5-H), 7.00 (d, 3-H), 7.34—7.49 (m, ph), and 2.03(s, CH_3CN); ^{31}P NMR ($(CH_3)_2CO$) **1a** 4.02. Yield **1a** 5 mg (3%).

X-Ray Data Analysis for $[Cu_2(\mu\text{-}Ph_2Ppy)_2(CH_3CN)_2](PF_6)_2$. The colorless crystal suitable for X-ray diffraction study was mounted on a Rigaku AFC-6B diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ=0.71073 Å). The conditions of data collection and the crystal data are listed in Table 1. A total of 3753 independent reflections having $F_o > 3\sigma(F_o)$ were used. The structure was solved by a direct method (MULTAN 78)[16] and refined by Block diagonal least-squares calculations with anisotropic thermal parameters including isotropic H atoms located on a difference Fourier synthesis, using the program system KPPXRAY.[17] Reliability factors are defined as $R=\sum(|F_o|-|F_c|)/\sum|F_o|$ and $R_w=\{\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2\}^{1/2}$, where $w=1/\sigma^2(F_o)$. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography, Vol. IV. The final R and R_w values were 0.067. Atomic coordinates of nonhydrogen atoms are given in Table 2.[18]

Results and Discussion

This section describes only the structure of **1a** because that of **1b** could not be determined by X-ray crystal analysis. The X-ray crystal structure of the complex **1a** is shown in Fig. 1. The complex consists of a centrosymmetric cation and noninteracting PF_6^- anions. Each copper atom is coordinated to one nitrogen atom of one Ph_2Ppy molecule and the nitrogen of CH_3CN, and one phosphorus atom of the other Ph_2Ppy molecule, resulting in a distorted trigonal geometry. The two copper atoms are bridged by two Ph_2Ppy molecules to form an eight-membered ring $Cu_2P_2N_2C_2$. The bridging mode of each Ph_2Ppy molecule is head-to-tail.[1-3,5,9] The most striking feature of the complex is that the eight-membered ring has a staggered conformation. To our knowledge, there is only one report of the conformation for $[Au_2(\mu\text{-dppm})_2Cl_2]$[12] in which the gold(I) atoms are three-coordinate. On the other hand, the dimetal complexes having a four-coordinate copper(I) atom[6,7,9] and silver(I) atom[8] give an eclipsed conformation. The complex **1a** and the Au(I) complex $[Au_2(\mu\text{-dppm})_2Cl_2]$ in which the central ions are three-coordinate give staggered conformations as described above. It was reported that the conformation of an eight-membered ring depends on the size and mode of binding of the other ligands which don't form part of the eight-membered ring.[8] In addition, the coordination numbers of the central metal ions are considered to be one of the most important factors governing the eight-membered ring conformation.

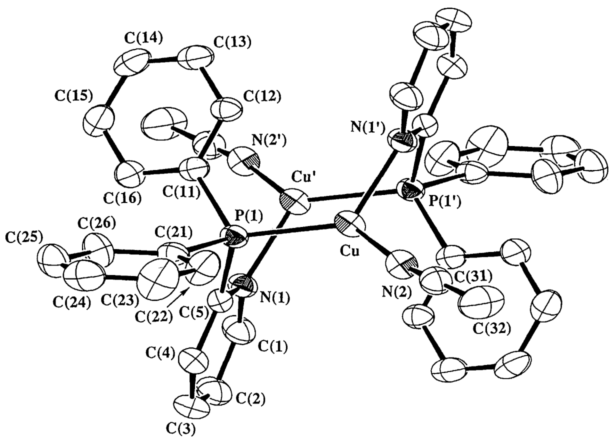

Fig. 1. ORTEP drawing of $[Cu_2(\mu\text{-}Ph_2Ppy)_2(CH_3CN)_2]^{2+}$ cations with 30% probability plots for thermal ellipsoids and atomic numbering. Half the atoms are labeled: the others are related by a center of inversion at the midpoint of the Cu···Cu′ vector. Only Cu′, P(1′), N(1′) and N(2′) in the coordination sphere are labeled. Selected bond distances (Å) and bond angles (°); Cu···Cu′=3.584(3), Cu-P(1)=2.204(2), Cu-N(2)=1.933(5), Cu-N(1′)=2.038(4), C(18)-N(2)=1.123(8), P(1)-Cu-N(2)=128.3(2), P(1)-Cu-N(1′)=120.0(1), N(2)-Cu-N(1′)=106.7(2), Cu-P(1)-C(5)=113.9(2), Cu-P(1)-C(11)=115.4(2), Cu-P(1)-C(21)=113.7(2), Cu-N(2)-C(31)=171.1(5).

The Cu-N(1′)(pyridyl) distance of 2.038(4) Å is slightly shorter than those (2.048(4)—2.114(4) Å) reported for three-coordinate copper(I) complexes.[5,9,19] It is interesting to note that the Cu-N(2)(CH_3CN) distance of 1.933(5) Å is between those (1.843(8)—1.846(10) Å) of three-coordinate copper(I) complexes[19] with CH_3CN and those (1.999(9)—2.161(3) Å) of four-coordinate copper(I) complexes[5,6] with CH_3CN. The Cu-P(1) distance of 2.204(2) Å is close to those (2.231(3)—2.296(8) Å) of copper(I) complexes with 1,1′-bis(diphenylphosphino)methane[6,20-22] and Ph_2Ppy.[5] The Cu···Cu′ distance of 3.584(3) Å is much longer than that (2.721(3) Å) of the analogous dicopper(I) complex[5] $[Cu_2(\mu\text{-}Ph_2Ppy)_3(CH_3CN)]^{2+}$.

The angles around copper(I) are P(1)-Cu-N(1′)=120.0(1), P(1)-Cu-N(2)=128.3(2), and N(2)-Cu-N(1′)=106.7(2)°, summing to 355.0°, since the copper atom lies 0.2661 Å from the plane defined by one phosphorus and two nitrogen atoms. The P(1)-Cu-N(1′) angle of 120.0(1)° is much smaller than the corresponding P-Au-P angle (155.9(1)°) of $[Au_2(\mu\text{-dppm})_2Cl_2]$[12] (the only complex reported to have a staggered conformation), while it is similar to those of eclipsed copper(I) complexes.[6,7]

^1H and ^{31}P NMR chemical shifts[23] of complex **1a** are shown in the experimental section. The ^1H NMR coordination shifts ($\Delta\delta=\delta_{complex}-\delta_{free}$) of the pyridine ring protons are 0.09—0.78 ppm, indicating the coordination of the nitrogen atom of Ph_2Ppy to Cu(I). On the other hand, the coordination shift of the CH_3 signal of CH_3CN was not observed within experimental error. This fact reveals the dissociation of a CH_3CN in acetone solution in contrast to the crystal structure. The ^{31}P NMR coordination shift of 7.70 ppm indicates the coordination of the phosphorus atom of the Ph_2P group to Cu(I). This value is significantly large when compared with other dinuclear complexes[2-4] with Ph_2Ppy and slightly larger than those of dinuclear complexes[6,12] with dppm.

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15) The structure of **1b** was identified as $[\mathrm{Cu_2}(\mu\text{-}\mathrm{Ph_2Ppy})_3(\mathrm{CH_3CN})](\mathrm{PF_6})_2$ by elemental analysis and the NMR method. ^{1}H NMR ($(\mathrm{CD_3})_2\mathrm{CO}$) $\delta=9.43$ (d, 6-H), 8.15 (t, 4-H), 7.92 (t, 5-H), 7.00 (d, 3-H), 7.33—7.48 (m, Ph), and 2.09 (s, $\mathrm{CH_3CN}$); ^{31}P NMR ($(\mathrm{CH_3})_2\mathrm{CO}$) 4.13. Found: C, 50.63; H, 4.44; N, 4.51%. Calcd for $\mathrm{Cu_2C_{53}H_{45}N_4P_5F_{12}}$ (**1b**): C, 51.00; H, 3.63; N, 4.48%. Yield: 32.5 mg (21%).

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23) ^{1}H and ^{31}P NMR chemical shifts ($(\mathrm{CD_3})_2\mathrm{CO}$) of free $\mathrm{Ph_2Ppy}$ and free $\mathrm{CH_3CN}$: ^{1}H NMR $\delta=8.67$ (d, 6-H), 7.69 (t, 4-H), 7.29 (t, 5-H), 7.09 (d, 3-H), and 7.40 (m, Ph) for $\mathrm{Ph_2Ppy}$, and 2.02 ($\mathrm{CH_3}$) for $\mathrm{CH_3CN}$; ^{31}P NMR $\delta=-3.68$ for $\mathrm{Ph_2Ppy}$.