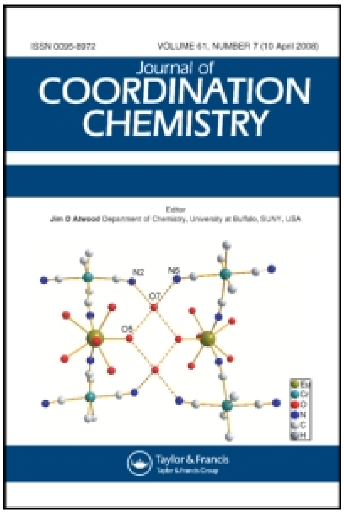

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Synthesis and crystal structure of a heterobinuclear complex $[(PhPPy_2)_2PdCuCl_2]ClO_4$ ($PhPPy_2$=bis(2-pyridyl)phenylphosphine)

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Synthesis and crystal structure of a heterobinuclear complex $[(PhPPy_2)_2PdCuCl_2]ClO_4$ ($PhPPy_2 = $ bis(2-pyridyl)phenylphosphine)

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The mononuclear palladium(II) complex *trans*-$[PdCl_2(PhPPy_2)_2]$ (**1**) reacts with $[Cu(CH_3CN)_4]ClO_4$ to afford the heterobinuclear $[(PhPPy_2)_2PdCuCl_2]ClO_4 \cdot 2CH_3CN$ (**2**), bridged by two $PhPPy_2$ ligands in a new mode. Complex **2** crystallizes in space group $P2_1/c$ with $a = 12.947(1)$, $b = 9.142(1)$, $c = 33.454(2)$ Å, $\beta = 99.698(1)°$. The copper(I) and palladium(II) ions in **2** adopt distorted tetrahedral and square-planar geometry, respectively. At room temperature, the complex is photoluminescent in solution.

Keywords: Palladium(II)–copper(I) complex; Crystal structure; 2-Pyridylphosphine ligand

1. Introduction

The coordination chemistry of 2-pyridylphosphine ligands $PPh_{3-n}(Py)_n$ ($n = 1$–3; Py = 2-pyridyl), has gained considerable attention in the past 30 years [1]. As a bridging ligand, Ph_2PPy has been widely used to construct homo- and hetero-binuclear complexes to study metal–metal bonding, focusing on the interaction between low-valent transition metal (Fe(0), Ru(0)), and metal atoms/or ions with d^{10} electronic configuration, such as Cu(I), Zn(II), Hg(II) [2]. Compared to Ph_2PPy, the coordination modes of bis(2-pyridyl)phenylphosphine ($PhPPy_2$) are complicated due to the increase of coordination atoms, not only acting as monodentate [3, 4], but also bidentate (chelating or bridging) [5–7] and tridentate (bridging) [3, 8]. Although there are several complexes reported containing $PhPPy_2$ ligands, including the crystal structures of $[RuCl(PPh_3)(PhPPy_2\text{-P, N,N}')]PF_6$ [8], *cis*-$[PhPPy_2]_2PdCl_2$ [4], *trans*-$Mo_2(\mu\text{-}O_2CCF_3)_2(O_2CCF_3)_2(PhPPy_2)_2$ [7] and $[(C_6F_5)_3Pt(\mu\text{-}PPhPy_2)Rh(COD)]$ [9],

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there are few reports on the interaction between high-valent transition metals, such as Pd(II), Pt(II), and metal ions with d^{1-10} electronic configurations [9]. In fact, interaction between these metals in polynuclear transition metal complexes is an important and exciting topic, due to the versatile chemical and physical properties that such complexes exhibit [10]. Recently a project was initiated to study self-assembly of polynuclear complexes and metal–metal bonding, by using *trans*-$PdCl_2(PhPPy_2)_2$ (**1**) as starting material. It is proposed that metal ions can be used to connect *trans*-$PdCl_2(PhPPy_2)_2$ molecules to form polynuclear complexes by coordination to free pyridyl groups in *trans*-$PdCl_2(PhPPy_2)_2$ with possible metal–metal interaction. In this article, a reaction of *trans*-$Pd(PhPPy_2)_2Cl_2$ (**1**) with $[Cu(CH_3CN)_4]ClO_4$ to give a new hetero-binuclear complex $[(PhPPy_2)_2PdCuCl_2]ClO_4$ (**2**) is described, not the expected polynuclear complex, in which $PhPPy_2$ exhibits a new coordination mode. Herein the synthesis and crystal structure of **2** as well as a convenient route to prepare $PhPPy_2$ are reported.

2. Experimental

2.1. *General details*

All synthetic procedures were performed under an atmosphere of dry argon using Schlenk techniques. Solvents were dried and distilled by standard methods. The chemicals and reagents were obtained commercially and used with further purification. The salt $[Cu(CH_3CN)_4][ClO_4]$ [11] and phenylphosphine ($PhPH_2$) [12] were prepared according to literature methods. ^1H NMR spectra were recorded on a Varian mercury-Vx 300 MHz instrument. Infrared spectra were recorded from KBr disks on a Bruker Equinox55 spectrometer in the region 400–4000 cm^{-1}. Ultraviolet and emission spectra were measured on a Perkin-Elmer UV-240 spectrometer and a HITACHI F-4500 Fluorescence Spectrophotometer, respectively.

2.2. *Synthesis of $PhPPy_2$*

Reaction of a suspension of lithium phenylphosphinidide ($PhPLi_2$), generated by treating $PhPH_2$ (1 mL, 0.009 mol) with 2 equiv. *n*-butyllithium (2.5 mol L^{-1}, 7.27 mL), with 2 equiv. 2-chloropyridine (1.72 mL, 0.018 mol) in benzene yielded a dark-red solution immediately, and finally a pale yellow suspension, from which $PhPPy_2$ was obtained as a pale yellow solid after purification (2.01 g, 83%). ^1H NMR (300 MHz, $CDCl_3$, ppm): 8.695 (2H, d, $J = 4.5$ Hz, Py), 7.1–7.7 (11H, m, Ph, Py).

2.3. *Synthesis of $[(PhPPy_2)_2PdCuCl_2]ClO_4$ (2)*

The mononuclear palladium(II) complex *trans*-$Pd(PhPPy_2)_2Cl_2$ (**1**) (20.2 mg, 0.028 mmol) prepared by reaction of *trans*-$Pd(PhNHEt)_2Cl_2$ [13] with $PhPPy_2$, and $[Cu(CH_3CN)_4]ClO_4$ (9.4 mg, 0.028 mmol) were dissolved in 5 mL dichloromethane to give an orange solution immediately. After stirring overnight at room temperature, a crude product was obtained as a pale yellow precipitate. Red-orange crystals of **2** (22.2 mg, 82.2%) were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the crude material. IR (KBr), ν (cm^{-1}): 1630, 1090, 623 (ClO_4^-); 1578, 1429, 3057 (Ph, Py). UV, λ_{max} (nm) ($\varepsilon/10^4\,dm^3\,mol^{-1}\,cm^{-1}$): 228 (0.911), 264 (0.663).

2.4. *X-ray diffraction study of 2*

Intensity measurements were collected on a Bruker Smart CCD diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). All calculations were performed using the SHELXTL package. The crystal structure was solved by direct methods and refined by full-matrix least squares. The detailed crystal data and structure refinement parameters are summarized in table 1.

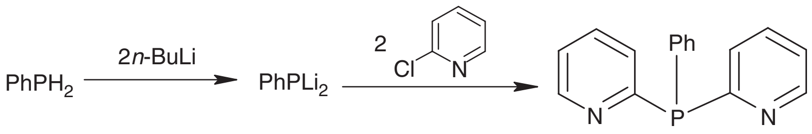
3. Results and discussion

3.1. *Synthesis*

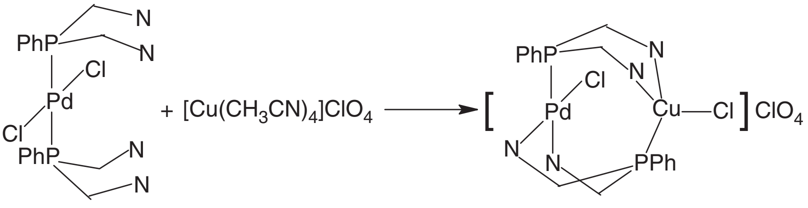
The heterobinuclear complex bis(2-pyridyl)phenylphosphine ($PhPPy_2$) was first prepared by Mann and Watson [14] from 2-pyridylmagnesium bromide and $PhPCl_2$ in low yield. Later Schmidbaur and Inoguchi [15] and Budnikova *et al.* [16] improved the yields to 39 and 68% by using complicated synthetic routes. In this work, treatment of diphenylphosphine with 2 equiv. *n*-BuLi yielded $PhPLi_2$, which subsequently reacted with 2 equiv. 2-chloropyridine to afford $PhPPy_2$ in 83% overall yield (scheme 1). Compared to methods in the literature, this one-pot synthetic route is convenient.

Table 1. Crystallographic data for $[(PhPPy_2)_2PdCuCl_2]ClO_4 \cdot 2CH_3CN$ (**2**).

Formula	$C_{36}H_{32}Cl_3CuN_6O_4P_2Pd$
F_w	950.94
Crystal system	Triclinic
Space group	$P2_1/c$
a, b, c (Å)	12.947(1), 9.142(1), 33.454(2)
α, β, γ(°)	90, 99.698(1), 90
V (Å^3)	3903.0(5)
T (K)	293(2)
Z	4
D_c ($mg\,m^{-3}$)	1.479
F(000)	1736
μ (mm^{-1})	1.331
Crystal size (mm^3)	0.40 × 0.36 × 0.20
hkl ranges	−10 to 17, −11 to 11, −43 to 41
Reflections collected/unique	23714, 9368
Data, parameters	9368, 480
R_1, wR_2	0.0592, 0.1282
Largest difference in peak and hole (e Å^{-3})	0.921, −0.414



Scheme 1. One-pot synthesis of ligand $PhPPy_2$.



Scheme 2. Synthesis of $[(PhPPy_2)_2PdCuCl_2]ClO_4$.

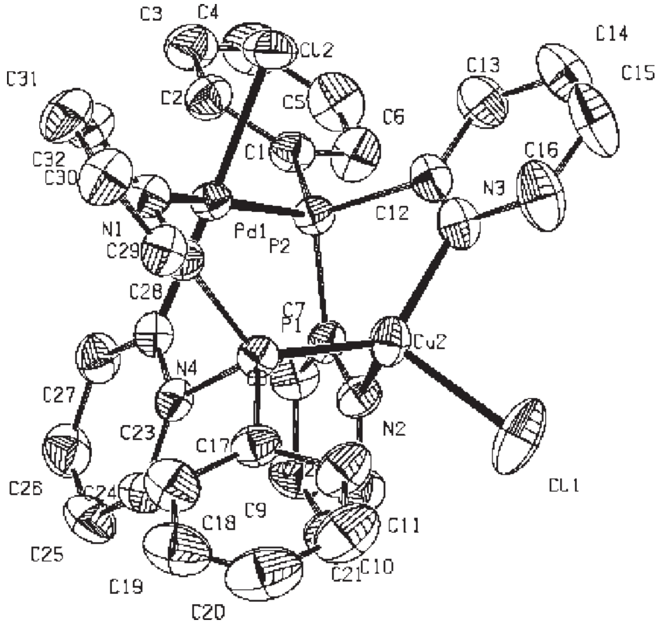


Figure 1. An ORTEP plot of the complex cation, $[(PhPy_2)_2PdCuCl_2]^+$, with crystallographic numbering scheme. The ClO_4^- anion and the hydrogen atoms are omitted for clarity.

Complex **1** was prepared from *trans*-$Pd(PhNHEt)_2Cl_2$ in a similar way to *trans*-$[Pd(dpnapy)_2Cl_2]$ [17]. Direct reaction of **1** with $[Cu(CH_3CN)_4]ClO_4$ yielded **2**, during which a color change was observed from yellow to orange. X-ray diffraction studies confirmed that in **2**, one palladium and one copper atoms are bridged by two *cis*-$PhPPy_2$ ligands to form a dinuclear complex (scheme 2). Each metal atom binds to one Cl, one P in $PhPPy_2$, and two N atoms from another $PhPPy_2$ ligand. Interestingly, one Cl atom and one $PhPPy_2$ in *trans*-$Pd(PhPPy_2)_2Cl_2$ have migrated from the Pd(II) to Cu(I), similar to that observed in preparation of $Pd_2(PhPPy_2)_2Cl_2$.

3.2. *Crystal structure*

The molecular structure of complex **2** was measured by single crystal X-ray crystallography. There is one perchlorate anion in this molecule, which is far from the cation of complex **2**, $[(PhPy_2)_2PdCuCl_2]^+$. The ORTEP plot of the complex cation is shown in figure 1, with selected bond lengths and angles in table 2. The coordination environment around the palladium atom in **2** is slightly distorted square planar, typical for

Table 2. Selected bond distances (Å) and angles (°) for **2**.

Bond distances			
Cu(2)–Cl(1)	2.302(2)	Pd(1)–Cl(2)	2.286(1)
Cu(2)–P(1)	2.217(1)	Pd(1)–P(2)	2.240(1)
Cu(2)–N(2)	2.159(4)	Pd(1)–N(1)	2.072(4)
Cu(2)–N(3)	2.061(4)	Pd(1)–N(4)	2.047(4)
Bond angles			
N(3)–Cu(2)–N(2)	91.92(15)	N(4)–Pd(1)–N(1)	87.19(14)
N(3)–Cu(2)–P(1)	132.63(12)	N(4)–Pd(1)–P(2)	95.36(10)
N(2)–Cu(2)–P(1)	107.10(11)	N(1)–Pd(1)–P(2)	164.82(11)
N(3)–Cu(2)–Cl(1)	100.15(13)	N(4)–Pd(1)–Cl(2)	177.41(11)
N(2)–Cu(2)–Cl(1)	98.30(11)	N(1)–Pd(1)–Cl(2)	90.65(11)
P(1)–Cu(2)–Cl(1)	118.61(6)	P(2)–Pd(1)–Cl(2)	87.09(4)

Pd(II) complexes. The angles of N(1)–Pd(1)–Cl(2) and N(1)–Pd(1)–P(2) are 177.41(11)° and 164.82(11)°, respectively. The Pd(1)–P(2) distance is 2.240(1) Å. The Pd–N distances are 2.072(4) Å and 2.047(4) Å, similar to Pd(III)–N distance (2.034 Å) in a dinuclear Pd(III) complex, $Pd_2(hpp)_4Cl_2$ [18], and shorter than Pd(II)–N (2.128 Å, 2.127 Å) in $Pd_2Cl_2(PPy_3)_2(MeO_2CC{=}CCO_2Me)_2CH_2Cl_2$ [6], indicating a strong interaction between Pd(II) and N atoms. In addition, the distance of Pd–Cl (2.286(1) Å) is short, compared to that of Pd(II)–Cl (2.357 Å, 2.349 Å) in *cis*-$Pd(PhPPy_2)Cl_2$ [4] and Pd(III)–Cl (2.474 Å) in $Pd_2(hpp)_4Cl_2$ [18]. The angles of N(3)–Cu(2)–P(1) 132.63(12)°, N(2)–Cu(2)–P(1) 107.10(11)°, N(3)–Cu(2)–Cl(1) 100.15(13)° and N(2)–Cu(2)–Cl(1) 98.30(11)° indicate that the copper(I) atom adopts a significantly distorted tetrahedral geometry. Two Cu–N distances are 2.061(4) Å for Cu(2)–N(3) and 2.159(4) Å for Cu(2)–N(2), close to the Cu–N bond lengths in $[Cu_3(\mu\text{-dpnapy})_3(CH_3CN)][ClO_4]_3$ (1.975–2.064 Å), $[Cu(bpy)(dpnapy)_2][ClO_4]$ (2.066 Å, 2.073 Å), and $[Cu_2(\mu\text{-dpnapy})_3][ClO_4]_2$ (2.106–2.239 Å) [19]. The bond length of Cu–P in **2** is 2.217 Å, slightly shorter than that found in $[Cu_2(\mu\text{-dpnapy})_3][ClO_4]_2$ (2.240 Å) [19]. The Cu–Cl distance of 2.3024(15) Å is normal, close to that in $[Cu_3(dpmp)_2(MeCN)_2(\mu\text{-Cl})_2]ClO_4$ (2.345–2.413 Å) [20]. In complex **2**, the long Pd(II) $\cdots$ Cu(I) (3.278 Å) distance indicates that there is no interaction between Pd(II) and Cu(I) metal ions.

In $PhPPy_2$-containing mononuclear complexes, the $PhPPy_2$ ligand coordinates to metals by phosphorus and/or nitrogen atoms as a monodentate ligand in $[Mo(CO)_5(PhPPy_2\text{-}P)]$, and a chelating ligand in $Mo(CO)_3(PhPPy_2)$ [3], $[Mo\{\eta^3\text{-allyl}\}Br(CO)_2(PhPPy_2\text{-}P,N)]$ [5] and $[MoI_2(CO)_3(PhPPy_2\text{-}N, N')]$ [3]. In oligomer $\{Mo(CO)_3(\mu\text{-}PhPPy_2)\}_n$ [3], it was proposed that P atom in $PhPPy_2$ coordinated to one Mo, and two N atoms in the same ligand bonded to another Mo atom, connecting $Mo(CO)_3(\mu\text{-}PhPPy_2)$ monomers to form an oligomer, based upon data from NMR and IR spectra [3]. In the crystal structure of complex **2**, clearly $PhPPy_2$ ligands coordinate to Pd(II) and Cu(I) in this new mode.

3.3. *Photoluminescent properties*

Numerous Cu(I)–phosphine complexes have been investigated for their luminescent properties [21]. At room temperature, complex **2** in acetonitrile displays photoluminescence (figure 2). The structureless emission band is located around 433 nm. For comparison, the emission spectra of free ligand and complex **1** were measured. Free ligand

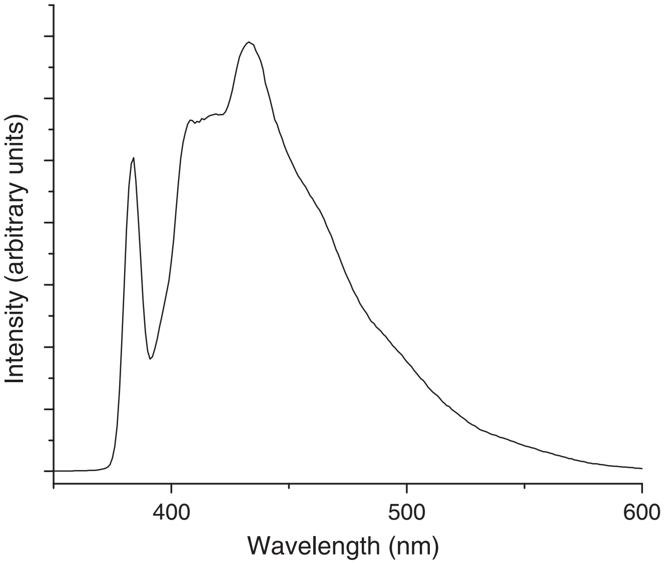


Figure 2. Emission spectrum of **2** in the acetonitrile solution at room temperature. Excitation wavelength 383 nm.

is photoluminescent ($\lambda_{\max}^{\text{em}} = 380\,\text{nm}$), and complex **1** exhibits similar emission to that of complex **2** except for its low intensity. The obtained data suggest that the luminescence is largely from a ligand localized excited state, and the coordination of palladium and copper perturbs the properties of the ligands, leading to the red-shift and increase in intensity of the emission [22, 23].

Supplementary data

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with the deposition number of CCDC 250536 for complex **2**. 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).

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