

**SYNTHESIS AND CHARACTERISATION OF SOME METAL COMPLEXES OF
HYBRID PHOSPHORUS-NITROGEN LIGANDS: THE CRYSTAL STRUCTURE OF
1-(DIPHENYLPHOSPHINO)-2-(2-PYRIDYL)ETHANE COBALT(II) CHLORIDE**

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ABSTRACT. Some iron(II), cobalt(II) and copper(II) complexes of the hybrid ligand 1-(diphenylphosphino)-2-(2-pyridyl)ethane (dppe) and diphenyl-2-pyridylphosphine (dppp) have been synthesised and characterised. Analyses suggest tetrahedral structures in which the metal atoms are bonded to two chlorine atoms and to both phosphorus and nitrogen atoms for 1-(diphenylphosphino)-2-(2-pyridyl)ethane on one hand and on the other hand, bonding is through the nitrogen atoms of two molecules of diphenyl-2-pyridylphosphine, which acts as a monodentate ligand. The crystal structure of 1-(diphenylphosphino)-2-(2-pyridyl)ethane cobalt(II) chloride shows a pseudo-tetrahedral structure in which the aminophosphine is bonded to the cobalt centre through both the phosphorus and nitrogen atoms, forming a 6-membered ring.

KEY WORDS: Aminophosphines, Metal complexes, Cobalt(II) complex, Crystal structure

INTRODUCTION

Transition metal complexes of tertiary phosphines have been extensively studied owing to the donor-acceptor properties of the phosphorus atom which provides enhanced coordination abilities of the ligands thus leading to complexes of high stability [1-4].

Some efforts in coordination chemistry research have recently been directed towards the study of metal complexes of the hybrid hemilabile P-N- [5-12], P-O- [13, 14] or P-S- [15-17] type ligands. This is due to their structural features, reactivity and catalytic properties resulting from the combination of a soft phosphine moiety with a hard oxygen- or nitrogen- donor functionality. Such hybrid ligands have been shown to display numerous ligating modes ranging from P- or N- coordination to the more common P- and N- bridging of two metal centres.

Some of these complexes display P- and N- chelation where the P- and N- donors of the ligands are simultaneously bonded to the same metal centre [5-12]. In this way they behave as hemilabile ligands with one arm, strongly bonded to the electron-rich transition metal centre and the other forming a weak bond with the metal, which can readily dissociate to generate a vacant site on the metal for the formation and/or stabilization of an intermediate species.

Most of the studies on metal complexes of phosphorus-nitrogen hybrid ligands have been focused on the second and third series of transition metals probably because of the large size of these atoms. Some complexes of the first row transition metals with these hybrid ligands have been reported but their structures have been established based on physical and spectroscopic measurements [5-7].

We report here on the syntheses and characterization of iron(II), cobalt(II) and copper(II) complexes of the hybrid ligand 1-(diphenylphosphino)-2-(2-pyridyl)ethane (dppe). The coordination ability of dppe is compared to that of dppp. The crystal structure of 1-(diphenylphosphino)-2-(2-pyridyl)ethane cobalt(II) chloride is also reported.

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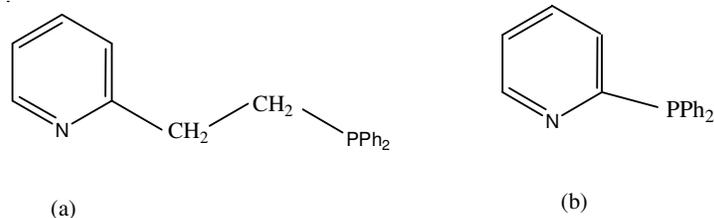


Figure 1. The ligands (a) 1-(diphenylphosphino)-2-(2-pyridyl)ethane, dppe, and (b) diphenyl-2-pyridylphosphine, dppp.

EXPERIMENTAL

Materials and preparations

All manipulations were performed under oxygen-free nitrogen atmosphere. All solvents used in this work were dried and distilled according to standard methods. All the metal salts (FeCl₂, CoCl₂·6H₂O and NiCl₂·6H₂O) were reagent grade and were used as supplied without further purification.

The ligand dppp (Aldrich) was used as purchased without further purification. The ligand dppe was synthesized using a modified procedure of the Uhlig and Maaser method [18]. A mixture of freshly-distilled vinyl pyridine (4.9 g, 46 mmol), diphenylphosphine (8.2 g, 44 mmol) and 2.0 mL of acetic acid were refluxed at 150 °C for 8 hours under nitrogen atmosphere. Methanol (75 mL) was added to dissolve the resulting yellowish oily product and the mixture neutralized with potassium carbonate and filtered to obtain a clear solution. Distilled water was then added until the solution became limpid. It was then stored overnight at -20 °C to obtain a colourless crystalline product which was filtered and dried in vacuum. The ligand is air-stable and soluble in most organic solvents.

³¹P-{NMR} = -19.3 ppm; ¹H-{NMR} = 2.5, 2.9, 7.0, 8.5 and 7.5 ppm; IR: 1591, 1568 cm⁻¹ (pyridine deformation). Analysis: % calculated for CoCl₂PNC₁₉H₁₈: C 78.35; H 6.19; N 4.81; found: C 78.82; H 6.28; N 4.12.

The metal complexes of dppp were prepared by adding an ethanolic solution of the ligand to a hot ethanolic solution of the metal salt in a 2:1 mole ratio and heating the resulting mixture while stirring for one hour. Complexes of dppe were also synthesized using a 2:1 ligand-to-metal mole ratio and the mixtures were heated under reflux for two hours. The products were filtered, washed with ethanol and dried in vacuo.

Instruments

Elemental analyses were performed by the Analyses Centre, Faculty of Pharmaceutical Science, University of Kanazawa, Japan and the metal analyses were performed on a Hitachi Z6100 Polarised Zeeman atomic absorption spectrophotometer. Infrared spectra were recorded as Nujol mulls using KBr pellets on a Horiba FT-200 spectrophotometer. Electronic spectra were recorded on a Hitachi U3500 spectrophotometer. Proton (¹H) and ³¹P {NMR} spectra were obtained on a JEOL JMTC 400 MHz spectrometer using CDCl₃ solution in 5 mm diameter tubes. ¹H spectra were referenced to TMS and ³¹P referenced to 85 % H₃PO₄ as external standards.

X-ray crystallographic studies

Crystals for X-ray analysis were grown by slow evaporation of an ethanolic solution of 1-(diphenylphosphino)-2-(2-pyridyl)ethane cobalt(II) chloride and a single crystal of ca. 0.1 x 0.1 x 0.1 mm in size was mounted on a glass fibre. All crystal data were collected on a Rigaku-RAXIS imaging plate area detector using graphite monochromated Mo-K α radiation ($\lambda = 0.71070$ Å) at a temperature of 288(1) K. The data were corrected for Lorentz and polarization effects.

Out of the 2433 measured reflections, the final cell parameters were obtained by full-matrix least squares refinement on 1646 observed reflections ($I > 4.00(I)$) and 217 variable parameters. The crystal and refinement data are given in Table 1. The structure was resolved by the direct method [19] and expanded using Fourier techniques [20, 21]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations but not refined. All calculations were performed using TEXSAN [21].

Additional material is available from the Cambridge Crystallographic Data Centre (Deposition number CCDC 652938).

Table 1. Crystal and refinement details for 1-(diphenylphosphino) 2-(2-yrldyl)ethane cobalt(II) chloride.

Formula	CoCl ₂ PNC ₁₉ H ₁₈
Mr	421.17
T/K	288(1)
Crystal system	triclinic
Space group	P-1(N ^o 2)
<i>Lattice parameters:</i>	
a/Å	10.20(2)
b/Å	8.68(2)
c/Å	15.98(2)
alpha/ ^o	72.07(8)
beta/ ^o	111.56(9)
gamma/ ^o	133.49(8)
V/Å ³	908.66
Z	2
D/mg m ⁻³	1.539
Crystal size/mm	0.1x0.1x0.1
$\mu/(\mu_0 - K_{\alpha})/\text{mm}^{-1}$	13.26
2 θ range/ ^o	54.0
Reflections measured	2433
Independent reflections	1646
N ^o of variables	217
R	0.095
R _w	0.133
Goodness of fit	2.28

RESULTS AND DISCUSSION

The ligand, 1-(diphenylphosphino)-2-(2-pyridyl)ethane is stable in air and soluble in most non-aqueous solvents. The infrared spectrum of dppe shows characteristic pyridine ring vibration frequencies at 1591 cm⁻¹ and 1567 cm⁻¹ while dppp show similar pyridine vibration frequencies at 1567 cm⁻¹ and 1560 cm⁻¹.

The ^{31}P {NMR} spectrum for dppe ligand exhibits the expected singlet at $\delta = -19.3$ in CDCl_3 . The ^1H {NMR} spectrum shows resonance at $\delta = 7.5$ attributed to phenyl protons and multiplets centred at $\delta = 2.9$ attributed to the protons of the CH_2CN_2 bridge.

Table 2 shows some physical properties and analytical data for Fe, Co, Ni complexes of dppp and dppe ligands. The analytical data for metal complexes of the dppp ligand show that the metal salts reacted with two equivalents of the ligand to yield complexes of the form $[\text{M}(\text{dppp})_2\text{Cl}_2]$, even when a 1:1 metal-to-ligand mole ratio was used. The infrared spectra of these complexes show pyridine ring deformation frequencies at ca. 1582 and 1557 cm^{-1} representing some shift from the free ligand values (1591 cm^{-1} and 1567 cm^{-1}). This suggests the formation of a metal-pyridine bond during the formation of the complex, with the phosphine moiety probably remaining uncoordinated. This monodentate coordination of the dppp ligand is expected from steric considerations.

Table 2. Analytical data for some metal complexes of P-N mixed ligands.

Compound	Colour	Yield (%)	IR data (cm^{-1}) pyridine deformation	Elemental analysis %, found (calc.)			
				% C	% H	% N	% Metal
$\text{Fe}(\text{dppe})\text{Cl}_2$	Cream	89.0	1601; 1569	54.90 (54.56)	4.45 (4.31)	3.26 (3.35)	12.45 (13.35)
$\text{Co}(\text{dppe})\text{Cl}_2$	Navy blue	85.8	1607; 1568	53.91 (54.28)	4.19 (4.29)	3.23 (3.33)	13.22 (13.99)
$\text{Ni}(\text{dppe})\text{Cl}_2$	Purple	86.8	1598; 1571	53.10 (54.20)	4.42 (4.28)	3.12 (3.33)	14.55 (13.94)
$\text{Fe}(\text{dppp})_2\text{Cl}_2$	Orange-red	35.5	1582; 1556	61.39 (62.44)	4.29 (4.28)	4.12 (4.28)	7.22 (8.52)
$\text{Co}(\text{dppp})_2\text{Cl}_2$	Deep blue	51.5	1583; 1556	61.70 (62.21)	4.35 (4.27)	4.09 (4.27)	8.75 (8.98)
$\text{Ni}(\text{dppp})_2\text{Cl}_2$	Orange-brown	69.8	1582; 1557	61.82 (62.22)	4.19 (4.27)	4.04 (4.27)	9.88 (8.94)
dppe	Colourless	-	1591; 1589; 1568; 1567	78.83 (78.35)	6.28 (6.19)	4.12 (4.81)	-
dppp	White	-	1567; 1560	-	-	-	-

Analytical data for metal complexes of the dppe ligand show a 1:1 metal-to-ligand ratio. These results were obtained even when one equivalent of the metal salt was reacted with two equivalents of the ligand. Infrared data show some shift in the pyridine ring deformation frequency for the coordinated ligand from 1589 and 1560 to ca 1600 and 1570 cm^{-1} , respectively. This suggests that dppe uses both P and N donor atoms for bonding.

The electronic spectra of these metal complexes show very intense absorption bands in the UV region ($\epsilon \approx 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) attributed to ligand transitions ($n \rightarrow \pi$; $\pi \rightarrow \pi^*$) and characteristic broad bands between 600 and 700 nm, attributed to $d \rightarrow d$ transitions ($\epsilon = 100\text{-}200 \text{ M}^{-1} \text{ cm}^{-1}$).

The ORTEP view of the crystal structure of 1-diphenylphosphine-2-(2-pyridyl)ethane cobalt(II) chloride is shown in Figure 2 together with the atom numbering scheme used in the corresponding tables while selected bond lengths and bond angles are presented in Table 3, respectively. The complex is found to crystallise in a triclinic crystal system, with space group $P\bar{1}(112)$ with $Z = 2$. The crystal packing of 1-diphenylphosphine-2-(2-pyridyl)ethane cobalt(II) chloride is shown in Figure 3. The cobalt atom is in a roughly tetrahedral environment, ligated to phosphorus, nitrogen and two chlorine atoms. The compound has a pseudo-tetrahedral structure in which the aminophosphine ligand coordinates to the cobalt centre through both the phosphorus and nitrogen atoms to form a 6-membered ring, giving a P1-Co-N bond angle of 98.8(2) °C. The carbon-carbon bond lengths of the phenyl rings range from 1.35(2) to 1.41(2), showing wide variations which suggest deformation of the phenyl rings on coordination. Bond angles about the metal atom range from 98.3 to 114.4, consistent with a distorted tetrahedral structure. The Co-N bond length of 2.068(2) is very similar to the values of 2.070(1) and 2.075(2) observed for $[\text{CoCl}_2(\text{NiT2Py})]$, a cobalt complex containing cobalt-pyridine bonding

[22]. The Co-Cl bond distances (2.221-2.244) is consistent with the Co-Cl values of 2.211(2)-2.252(3) reported for $[(\text{CoClPh}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]$ [23]. The Co-P bond length of 2.387(5) is slightly longer than that observed in cobalt tertiary phosphine complex, $[\text{Co}(\text{PMe}_3)_2]$ with a Co-P bond length of 2.28-2.28 [24]. This lengthening might be due to a weaker donor ability of the P-, N-donors in the aminophosphines.

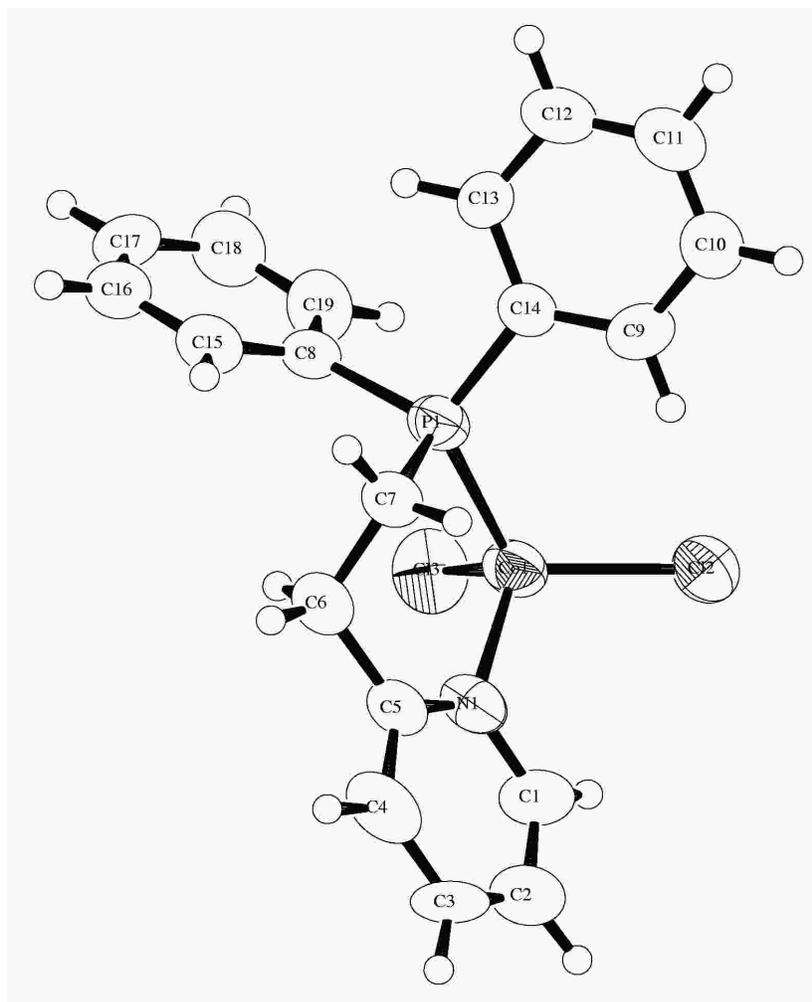


Figure 2. Ortep drawing of the crystal structure of 1-(diphenylphosphino)-2-(2-pyridyl)ethane cobalt(II) chloride. (H-atoms omitted for clarity).

Table 3. Selected bond lengths (Å) and bond angles (°) for 1-diphenylphosphino(2-(2-pyridyl)ethane)cobalt(II) chloride.

Bond lengths (Å)					
Atom	Atom	Distance	Atom	Atom	Distance
Co(1)	Cl(2)	2.244(4)	Co(1)	Cl(3)	2.221(5)
Co(1)	P(1)	2.387(3)	Co(1)	N(1)	2.068(8)
P(1)	C(7)	1.811(10)	P(1)	C(8)	1.84(1)
P(1)	C(14)	1.807(10)	N(1)	C(1)	1.36(1)
N(1)	C(5)	1.34(1)	C(1)	C(2)	1.38(2)
C(2)	C(3)	1.35(2)	C(3)	C(4)	1.40(2)
C(4)	C(5)	1.43(1)	C(5)	C(6)	1.55(2)
C(1)	H(1)	0.96	C(2)	H(2)	0.99
C(3)	H(3)	0.96	C(4)	H(4)	0.97

Bond angles (°)							
Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
Cl(2)	Co(1)	Cl(3)	114.4(2)	Cl(2)	Co(1)	P(1)	113.6(1)
Cl(2)	Co(1)	N(1)	104.7(3)	Cl(3)	Co(1)	P(1)	110.8(2)
Cl(3)	Co(1)	N(1)	113.8(2)	P(1)	Co(1)	N(1)	98.3(3)
Co(1)	P(1)	C(7)	102.4(4)	Co(1)	P(1)	C(8)	114.5(3)
Co(1)	P(1)	C(14)	121.1(4)	C(7)	P(1)	C(8)	106.3(5)
C(7)	P(1)	C(14)	106.0(4)	C(8)	P(1)	C(14)	105.3(5)
Co(1)	N(1)	C(1)	114.3(7)	Co(1)	N(1)	C(5)	127.7(7)
C(1)	N(1)	C(5)	117.9(8)	N(1)	C(1)	C(2)	123(1)
C(1)	C(2)	C(3)	119(1)	N(1)	C(5)	C(4)	120(1)
C(2)	C(3)	C(4)	118.5(9)	N(1)	C(1)	H(1)	116.2
P(1)	C(7)	C(6)	113.3(6)	C(1)	C(2)	H(2)	120.2
P(1)	C(8)	C(15)	123.2(7)	C(2)	C(1)	H(1)	119.8
P(1)	C(8)	C(19)	117.5(8)	C(11)	C(10)	H(6)	119.9
P(1)	C(7)	H(17)	110.5	C(9)	C(10)	H(6)	121.3
P(1)	C(7)	H(18)	109.7	C(14)	C(9)	H(5)	119.5
H(15)	C(6)	H(16)	107.4	C(10)	C(9)	H(5)	119.6

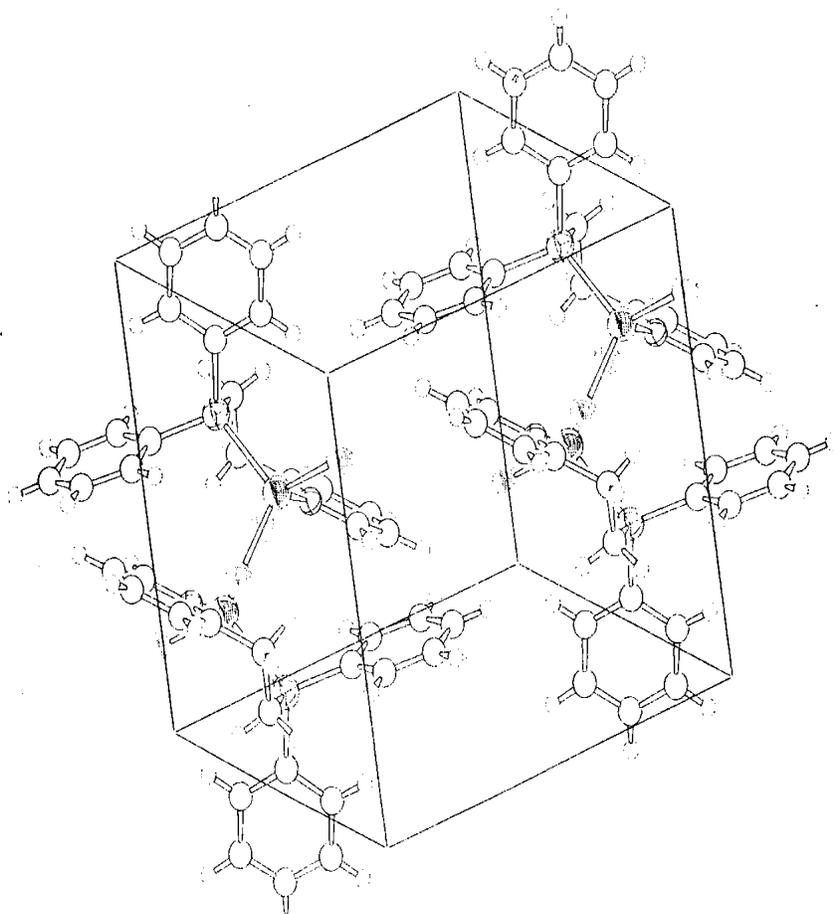


Figure 3. Crystal packing for 1-(diphenylphosphino)-2-(2-pyridyl)ethane cobalt(II) chloride.

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