

Synthesis and Characterization of Cobalt(II) Complexes with Hemilabile P[^]N Donor Ligands

RAJJYOTI GOGOI*, CHANDAN PATHAK and GEETIKA BORAH

Department of Chemistry, Dibrugarh University, Dibrugarh-786004, India

*Corresponding author: E-mail: rajyotigogoi99@gmail.com

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Two cobalt(II) complexes viz. $\text{CoCl}_2\{\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)\}_2$ (C_1) and $\text{CoCl}_2(\text{PPh}_2\text{Py})_2$ (C_2) were synthesized by reacting $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 4-(dimethylamino)phenyldiphenylphosphine and diphenyl-2-pyridylphosphine ligands, respectively. The complexes were characterized by elemental analysis, FT-IR, UV-visible and electronic spin resonance (ESR) spectroscopic technique. Both the complexes were found stable at room temperature. EPR measurements and UV-visible spectra analysis of C_1 and C_2 are consistent with a tetrahedral Co(II) and tetragonally distorted octahedral Co(II) ions, respectively.

Keywords: Cobalt, Ligand, 4-(Dimethylamino)phenyldiphenylphosphine, Diphenyl-2-pyridylphosphine, Tetragonal.

INTRODUCTION

Transition metal complexes containing hemilabile ligand have received considerable attention because of their unusual structural features, versatile binding modes and biological implications [1-7]. Different types of hemilabile ligands such as P-O, P-S, P-N *etc.* and their transition metal complexes have been reported. Hemilabile ligands have several distinct advantages over the homo functional ligands [8,9]. Aminophosphines can make the metal centre more electron rich by direct M-P or M-N interaction. Due to this reason they have greater ability to undergo oxidative addition and reductive elimination reactions and found tremendous catalytic applications in homo and heterogeneous systems for different reactions such as hydrogenation, hydroformylation, carbonylation, transfer hydrogenation, cross-coupling reaction *etc.* [10-17]. It can bind to the metal atom in a number of fashions depending upon the structure of the ligand and the oxidation state of the metal. The P-donor can stabilize the metal in their low oxidation state, while N-donor can create a vacant coordination site for substrate binding. These ligands have important applications in supramolecular chemistry also.

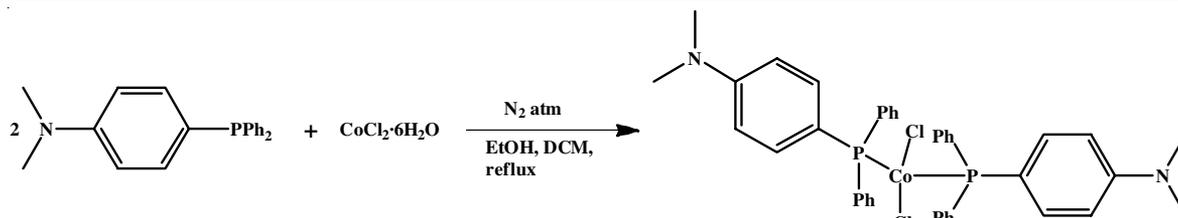
Aydemir and co-workers [1] have reported Rh(I), Ru(II), Ir(III) complexes of aminophosphines and found promising catalytic activity in transfer hydrogenation reaction. The phosphinoamine chemistry of 4*d*- and 5*d*-transition metals are more

developed than the 3*d*-transition metal ions, probably because of the large size of these atoms. Few monodentate and bidentate cobalt complexes of P[^]N ligands have been reported which exhibited diverse steric and electronic properties [18,19]. Some of them have rigid back bond and some other have flexible alkyl chain that join the two/three donor atoms. Moreover, few complexes of Fe, Au, Ag and W with diphenyl-2-pyridylphosphine and 4-(dimethylamino)phenyldiphenylphosphine ligands have also been reported [20-23]. Our interest in the present work is to extend the boundary-line of the phosphinoamine chemistry towards 1st row transition metals and herein we report the synthesis of Co(II) complexes with 4-(dimethylamino)phenyldiphenylphosphine and diphenyl-2-pyridylphosphine ligands and characterization of these complexes.

EXPERIMENTAL

All the reagents used in the synthesis of the complexes were of AR grade. The metal precursor ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was used without further purification. All organic solvents such as ethanol, DCM, DMSO *etc.* used in the present work were purchased from Merck and were distilled according to standard procedure. The ligands, diphenyl-2-pyridylphosphine and 4-(dimethylamino)phenyldiphenylphosphine were purchased from Sigma Aldrich and used as received.

FT-IR spectra were recorded in KBr pellets on Shimadzu IR prestige-21 FT-IR spectrophotometer (4000-200 cm^{-1}). The

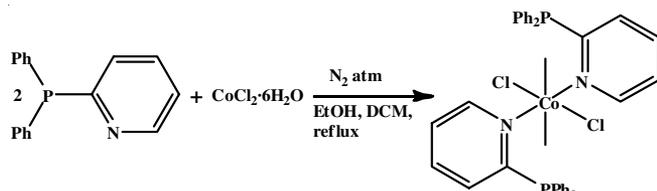


Scheme-I: Synthesis of the complex $[\text{CoCl}_2\{\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)\}_2]$ (C_1)

ESR spectra of the complexes were recorded at liquid nitrogen temperature in X-band region at IIT, Madras, India. The electronic spectra of the complexes were recorded in DCM solution in the range 200–800 nm with a Graphicord UV-240 (Shimadzu), UV-1700 spectrophotometer. ^1H and ^{31}P NMR were recorded in DMSO- d_6 using TMS as an internal standard on a Bruker Avance 400 MHz spectrometer. The C, H and N analysis were done with a Perkin-Elmer 2400 Series II C,H,N analyzer. Melting point of the complexes were recorded with a Buchi B 450 melting point apparatus.

Synthesis of $[\text{CoCl}_2\{\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)\}_2]$ (C_1): 1 mmol (0.51 g) $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ dissolved in 10 mL ethanol was added to a solution of 4-(dimethylamino)phenyldiphenylphosphine prepared by dissolving 2 mmol (0.84 g) of the ligand in 10 mL DCM. The reaction mixture was then refluxed under N_2 atm for 3 h with constant stirring. The resulting mixture was evaporated under reduced pressure whereupon a solid mass was obtained (**Scheme-I**). It was washed with ether and dried. Finally a dark green solid was obtained. Found (calcd.): C, 66.52 (67.17); H, 5.40 (5.74); N, 4.07 (3.71) for $\text{CoCl}_2\{\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)\}_2$. m.p. 161 °C. IR (KBr, ν_{max} , cm^{-1}): 1436 (C-N), 432 (Co-P), 343 (Co-Cl).

Synthesis of $[\text{CoCl}_2(\text{PPh}_2\text{Py})_2]$ (C_2): 2 mmol (0.53 g) Diphenyl-2-pyridylphosphine and 1 mmol (0.51 g) $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ was dissolved separately in 10 mL DCM and 10 mL ethanol, respectively and was mixed slowly with stirring. The reaction mixture was refluxed for 3 h with constant stirring under N_2 atmosphere. The solvent was then evaporated under vacuum and the resulting solid mass was washed with ether and dried in vacuum (**Scheme-II**). Finally a dark green solid was obtained. Found (calcd.) C, 63.05 (62.99); H, 4.1 (4.99); N, 3.91 (4.08) for $\text{CoCl}_2(\text{PPh}_2\text{Py})_2$. m.p. 154 °C. IR (KBr, ν_{max} , cm^{-1}): 1431 (py(C=N)), 520 (Co-N), 440 (Co-P), 332 (Co-Cl).



Scheme-II: Synthesis of the complex $[\text{CoCl}_2(\text{PPh}_2\text{Py})_2]$ (C_2)

RESULTS AND DISCUSSION

The melting point of the complexes C_1 and C_2 are found to be 161 °C and 154 °C, respectively, which are different from the melting point of the starting materials $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (m.p.: 110 °C) and the respective ligands $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$ (d.p. 151–154 °C) and PPh_2Py (m.p.: 85 °C), indicating the formation of the new complexes C_1 and C_2 . The complexes are dark green

in colour and soluble in common organic solvents *viz.* dichloromethane, tetrahydrofuran, DMSO *etc.* and were found stable under ambient conditions.

FT-IR study: The $\nu(\text{C-N})$ stretching frequency for the complex, C_1 was observed at 1436 cm^{-1} which was almost equal to the $\nu(\text{C-N})$ stretching frequency value of the free ligand, indicating that the $-\text{NMe}_2$ did not take part in the complexation. A weak band at 432 cm^{-1} and a moderate intensity band at 343 cm^{-1} could be assigned to Co-P and Co-Cl stretching vibrations, respectively [5]. In the IR spectrum of C_2 a sharp band at 1431 cm^{-1} was attributed to the $\nu_{\text{py}}(\text{C=N})$ vibration. This band showed a significant downfield shift compared to the free ligand PPh_2Py , indicated coordination through N-atom. The complex C_2 exhibited moderate intensity peaks at 520, 440 and 332 cm^{-1} attributable to Co-N, Co-P and Co-Cl vibrations, respectively [3,4].

UV-visible spectral analysis: In the UV-visible spectrum of complex C_1 (Fig. 1a) an absorption at 405 nm could be assigned to intra ligand $n\rightarrow\pi^*$ transition. The bands at 720 and 632 nm could be tentatively attributed to $^4\text{A}_2(\text{F})\rightarrow^4\text{T}_1(\text{F})$ and $^4\text{A}_2(\text{F})\rightarrow^4\text{T}_1(\text{P})$ transitions, respectively. The splitting of peak at 632 nm may be due to distortion from regular symmetry. The complex C_2 demonstrated two peaks at 650 and 587 nm assignable to the transitions $^4\text{T}_{1g}(\text{F})\rightarrow^4\text{A}_{2g}(\text{F})$ and $^4\text{T}_{1g}(\text{F})\rightarrow^4\text{T}_{1g}(\text{P})$, respectively (Fig. 1b). Appearance of a hump peak at 700 nm clearly indicates Jahn-Teller distortion in the complex [24]. UV-visible spectral analysis indicates distorted tetrahedral geometry and octahedral geometry (Jahn-Teller distortion) for the complexes C_1 and C_2 , respectively.

ESR analysis: The ESR spectra of both complexes C_1 and C_2 were recorded at liquid N_2 temperature in magnetically dilute form. The complex C_1 exhibited three g values at 4.91, 3.62 and 2.45, which is attributed to tetrahedral symmetry around the metal ion. A tetrahedral Co(II) would result in a ground $S = 3/2$ state, so is a Kramers ion and due to zero field splitting should show three EPR signals (Fine splitting) [25]. On the other hand, two g values at 2.77 (g_{\parallel}) and 1.83 (g_{\perp}) for the complex C_2 is indicative of tetragonally distorted octahedral environment around the cobalt ion [26].

(^1H and ^{31}P) NMR analysis: Since the complexes are paramagnetic, so their NMR spectra could not be resolved.

Conclusion

We have successfully synthesized monometallic two Co(II) complexes of the rigid backbone 4-(dimethylamino)-phenyldiphenylphosphine and flexible diphenyl-2-pyridylphosphine ligands. The complexes C_1 and C_2 were tentatively assigned a tetrahedral and tetragonally distorted octahedral geometry, respectively.

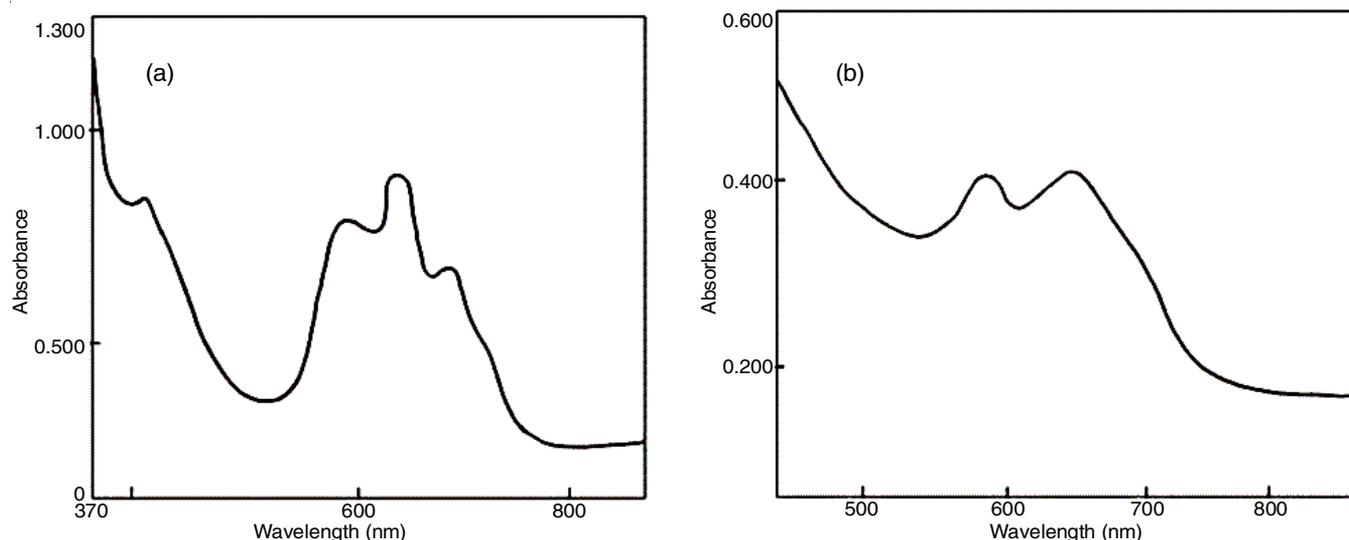


Fig. 1. Electronic absorption spectrum of (a) $\text{CoCl}_2\{\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)\}_2$ (C_1) and (b) $\text{CoCl}_2(\text{PPh}_2\text{Py})_2$ (C_2) complexes

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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