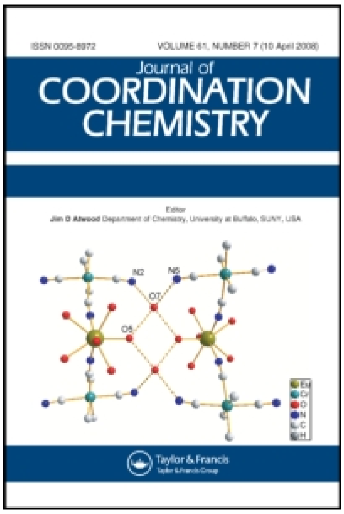

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<i>Bis</i>-(3,5-dimethyl-pyrazolyl-1-methyl)-(3-phosphanyl-propyl)-amine complexes of copper(II), nickel(II), and cobalt(II)

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Bis-(3,5-dimethyl-pyrazolyl-1-methyl)-(3-phosphanyl-propyl)-amine complexes of copper(II), nickel(II), and cobalt(II)

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A series of Cu(II), Co(II), and Ni(II) complexes of *bis*-(3,5-dimethyl-pyrazolyl-1-methyl)-(3-phosphanyl-propyl)-amine $C_{15}H_{26}N_5P$ (**1**), prepared from 3-aminopropylphosphine and 1-hydroxymethyl-3,5-dimethylpyrazole were characterized. The nature of bonding and the geometry of the complexes have been deduced from elemental analysis, infrared, electronic, ^1H NMR, ^{31}P NMR spectra, magnetic susceptibility, and conductivity measurements. The studies indicate octahedral geometry for nickel complex and square pyramidal geometry for copper and cobalt complexes. The EPR spectra of copper complex in acetonitrile at 300 K and 77 K were recorded. Biological activities of the ligand and metal complexes have been studied on *Staphylococcus aureus*, *Escherichia coli*, *Aspergillus niger*, and *Aspergillus flavus* by well-diffusion method. The zone of inhibition values were measured at 37°C for a period of 24 h. The electrochemical behavior of copper complexes was studied by cyclic voltammetry. Catalytic study indicates the copper complex has efficient catalytic activity in oxidation of amitriptyline.

Keywords: 3-Aminopropylphosphine; 1-Hydroxy-3,5-dimethylpyrazole; Metal complexes; Catalytic activity

1. Introduction

Transition-metal compounds derived from functionalized phosphines have broad use in homogeneous catalysis [1–3]. Systematic variation of substituents on P^{III} is an effective tool for tuning of electronic effects in phosphine ligands and in their corresponding transition-metal complexes. The substituents define the cone angle around the P^{III} center, which plays an important role in catalytic activity of metal complexes [4–6]. Therefore, functionalization and fine tuning of substituents around P^{III} centers is of continued interest in the overall design and development of phosphine ligands for transition-metal-based homogeneous catalysts. Pyrazole-containing ligands and their metal complexes possess a wide spectrum of medicinal properties. These interesting features led us to study the present system.

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2. Experimental

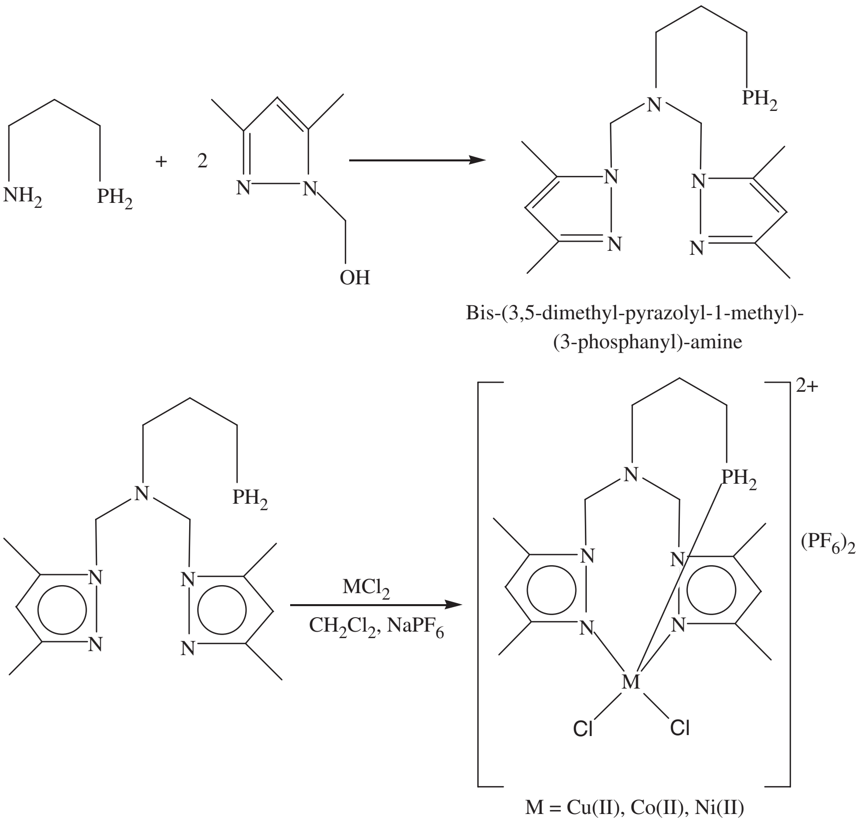
All chemicals were obtained from Aldrich Chemical & Co. and used without purification. All reactions were carried out under nitrogen. The UV–Vis spectra of the ligand and metal complexes were recorded in dichloromethane using a JASCO V-530 spectrophotometer. Infrared (IR) spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer in Thiagarajar College, Madurai. Cyclic voltammetry measurements were carried out at room temperature in acetonitrile under N_2 (Model BAS-50 voltammograph) using a three electrode cell containing a reference Ag/AgCl electrode, Pt wire auxiliary electrode and glassy carbon working electrode in acetonitrile with Tetrabuthylammonium Perchlorate (TBAP) as supporting electrolyte. Elemental analyses were performed at CDRI, Lucknow. ^1H NMR spectra were recorded in $CDCl_3$ using a Bruker DRX-300, 300 MHz NMR spectrometer. ^{31}P NMR spectra were recorded with a 161 MHz spectrometer using $CHCl_3$ as a solvent and 85% H_3PO_4 as the external reference, at IISc Bangalore. Electron Spin Resonance (ESR) spectra were recorded in solid state at 300 K and 77 K with a JEOL TES 100 ESR spectrometer; magnetic moments of the complexes were measured by VSM model 7404 at Pondicherry University. Effective magnetic moments were calculated using the formula $\mu_{\mathrm{eff}} = 2.228\ (\chi_{\mathrm{M}}T)^{1/2}$, where χ_{M} is the corrected molar susceptibility. Molar conductances of the complexes were measured in methanol at room temperature using a Systronic conductivity bridge type (OSWAL).

2.1. *Preparation of* bis-*(3,5-dimethyl-pyrazolyl-1-methyl)-(3-phosphanyl-propyl)-amine (1)*

To 2.94 g (32.5 mmol) of 3-aminopropylphosphine dissolved in 20 mL dichloromethane was added 8.20 g (65.0 mmol) of 3,5-dimethylhydroxymethylpyrazole in 15 ml dichloromethane. This mixture was stirred for half an hour and allowed to stand for 48 h. The solvent was evaporated under reduced pressure and the product was obtained as a colorless viscous oil. Elemental analysis (Found: C, 58.24; H, 8.07; N, 22.27; $C_{15}H_{26}N_5P$. Calculated: C, 58.61; H, 8.53; N, 22.78.) $\upsilon_{\max}$ (KBr) cm^{-1} 1654 (C=N), 1225 (P–H); ^1H NMR δ(300 MHz; $CDCl_3$), 2.79 (12H, s, CH_3), 5.84 (2H, s, Py–H), 1.4 (2H, m, CH_2CH_2–CH_2), 2.36 (2H, t, N–CH_2–CH_2–CH_2, $J = 6.3$ Hz), 1.3 (2H, t, CH_2–CH_2–CH_2–PH_2, $J = 6.9$ Hz), 4.8(4H, S, N–CH_2–N). ^{31}P NMR shows signal (161 MHz; $CHCl_3$) at −144.5 ppm due to the primary phosphine moiety.

2.2. *Preparation of metal complexes*

To 3.073 g (10 mmol) of *bis*-(3,5-dimethyl-pyrazolyl-1-methyl)-(3-phosphanyl-propyl)-amine dissolved in 25 ml of dichloromethane was added 10 mmol of MCl_2 (M = Cu(II), Co(II), Ni(II)). To this mixture 0.335 g (2 mmol) of sodium hexafluorophosphate and a small amount of triethylamine was added and the reaction mixture was stirred for 6 h. The solvent was reduced to a small volume, and addition of petroleum ether precipitated metal complexes which were filtered, washed with ether, and dried under vacuum (scheme 1).



Scheme 1. Synthesis of ligand and metal complexes.

3. Results and discussion

The synthon 3-aminopropylphosphine was obtained through Arbuzov reaction of 1,3-dibromopropane with triethylphosphite followed by conversion of the diethyl-3-bromopropylphosphonate to the corresponding azide (diethyl-3-azidopropylphosphonate), which upon reduction with lithium aluminum hydride gave 3-aminopropylphosphine. It was nonpyrophoric acid and moderately stable in air, but stored in nitrogen [7–9].

In this work, *bis*-(3,5-dimethyl-pyrazolyl-1-methyl)-(3-phosphanyl-propyl)-amine (**1**) was prepared by reaction of 3-aminopropylphosphine with 1-hydroxy-3,5-dimethylpyrazole in a 1 : 2 molar ratio. Ligand **1** shows oxidative stability in the absence of bulky substituents. Almost all the reported crystal structure of free primary monophosphines contain bulky groups attached to the phosphorus to render stability to P–H bonds [10–16]. The reason for the unusual oxidative stability of **1** is unclear. However, earlier work of Gali *et al.* [17], Prabhu *et al.* [18], Pillarsetty *et al.* [19], and Brauer *et al.* [20] suggest that electronegative heteroatoms such as nitrogen or sulfur, two or three carbons away from the phosphorus, may have negative hyper conjugative electronic influence on the P^{III} centers rendering the primary phosphine oxidatively stable [17, 19].

The elemental analysis data of the ligand and their metal complexes are presented in table 1 with estimated values in good agreement with theoretical. The analytical data of the metal complexes indicate general formula MLX_2 for metal : ligand ratio 1 : 2. All the complexes are air stable, non-hygroscopic, and high melting. The low molar conductance values of the complexes in dichloromethane reveal their non-electrolytic nature.

3.1. *Electronic spectra*

The electronic spectra of the ligand and metal complexes are presented in table 2. The absorption spectrum of **1** exhibits a strong peak in the UV range, centered at 25,189 cm^{-1} due to charge transfer. Strong peaks in the UV range of solutions of complexes indicate charge transfer between the ligands and the central ion. The electronic spectrum of Cu(II) complex showed bands at 10,798, 14,814, and 18,643 cm^{-1}, tentatively assigned to $^2B_1 \rightarrow {}^2A_1(\nu_1)$, $^2B_1 \rightarrow {}^2B_2$ (ν_2), and $^2B_1 \rightarrow {}^2E(\nu_3)$, respectively, characteristic of square pyramidal geometry [21, 22]. Co(II) complex displayed bands at 10,964, 17,543, and 19,880 cm^{-1} assigned to $^4A_2 + {}^4E \rightarrow {}^4B_1$, $^4A_2 + {}^4E \rightarrow {}^4E(P)$, and $^4A_2 + {}^4E \rightarrow {}^4A_2(P)$, also characteristic of square pyramidal geometry [22]. Ni(II) complex showed absorption bands at 10,309, 15,873, and 23,866 cm^{-1}, and these bands may be tentatively assigned as $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2), and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions suggesting octahedral geometry [22].

Table 1. Elemental analysis data and colors of the ligand and their metal complexes.

		Calculated (%)				Found (%)				
Compounds	Color	M	C	H	N		C	H	N	m.p. °C
$C_{15}H_{26}Cl_2N_5P(PF_6)_2$	Colorless	–	58.61	8.53	22.78	–	58.24	8.07	22.27	–
$[Cu(C_{15}H_{26}N_5Cl_2P)](PF_6)_2$	Green	8.68	24.62	3.58	9.57	8.10	24.24	3.17	9.19	288
$[Co(C_{15}H_{26}N_5Cl_2P)](PF_6)_2$	Blue	8.10	24.78	3.60	9.63	7.92	24.32	3.09	9.17	220
$[Ni(C_{15}H_{26}N_5Cl_2P)](PF_6)_2$	Greenish yellow	8.07	24.78	3.61	9.63	7.85	24.35	3.07	9.28	>300

Table 2. Electronic spectral data and magnetic moments for ligand and their metal complexes.

Compounds	Frequency (cm^{-1})	Transition	Geometry	μ_{eff}(BM)
$C_{15}H_{26}N_5P$	25,189	Charge transfer	–	–
	47,169			
$[Cu(C_{15}H_{26}N_5Cl_2P)](PF_6)_2$	10,798	$^2B_1 \rightarrow {}^2A_1(\nu_1)$	Square pyramidal	1.40
	14,814	$^2B_1 \rightarrow {}^2B_2(\nu_2)$		
	18,643	$^2B_1 \rightarrow {}^2E(\nu_3)$		
$[Co(C_{15}H_{26}N_5Cl_2P)](PF_6)_2$	10,964	$^4A_2 + {}^4E \rightarrow {}^4B_1$	Square pyramidal	4.69
	17,543	$^4A_2 + {}^4E \rightarrow {}^4E(P)$		
	19,880	$^4A_2 + {}^4E \rightarrow {}^4A_2(P)$		
$[Ni(C_{15}H_{26}N_5Cl_2P)](PF_6)_2$	17,762	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	Octahedral	2.17
	15,873	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$		
	23,866	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$		

3.2. *Magnetic susceptibility*

Magnetic susceptibility values are shown in table 2. The copper complex at 1.40 B.M. is considerably lower than the spin only value of copper complexes. Co(II) and Ni(II) complexes have magnetic moment values 4.69 and 2.17 B.M., respectively, also lower than the respective spin only values due to mixing of orbital angular momentum from excited state via spin–orbit coupling [23].

3.3. *IR spectra*

IR spectrum of free ligand was compared with spectra of their metal complexes (table 3). The IR spectrum of **1** shows bands at 2285, 1636, and 1281 cm^{-1} due to υ(P–H), υ(C=N) and υ(N–N), respectively. The υ(P–H) vibration shifted to lower frequency indicates that P is coordinated with metal. The band at 1636 cm^{-1} assigned to pyrazole ring nitrogen group of ligand and is shifted to lower frequency after complexation indicating coordination of ring nitrogen to metal [24, 25]. Proof of N and chloride coordination is demonstrated by new bands at 427–442 and 318–342 cm^{-1} assigned as ν(M–N) and ν(M–Cl). The strong absorption at 838–846 cm^{-1} corresponds to $[\mathrm{PF}_6]^-$ [26].

3.4. *ESR spectra*

A powder ESR spectrum of copper(II) complex was recorded at room temperature using 2,2-diphenyl-1-picrylhydrazyl (DPPH) as a reference standard. The spectrum appeared to be slightly broadened with $g_{\perp} = 2.0201$ and $g_{\parallel} = 2.256$, characteristic of square pyramidal geometry. The observed $g_{\parallel}$ value (2.256) for the complex is less than 2.3 suggesting significant covalent character of the metal–ligand bond in agreement with the observation of Kivelson and Neiman [27]. By observing g-values it is clear that $g_e < g_{\perp} < g_{\parallel}$ $(2.0023 < 2.020 < 2.256)$ suggesting that $d_{x^2-y^2}$ orbital is the ground state and the d^9 configuration is $(eg)^4(a_{1g})^2(b_{2g})^2(b_{1g})^1$. The '$g$' values are related to the axial symmetry [28] and $g_{\parallel} > g_{\perp}$ suggests square pyramidal geometry for Cu(II), also supported by the unpaired electron lying predominately in $d_{x^2-y^2}$ as evident from the value of the exchange interaction term G, estimated from the expression,

$$G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$$

If $G > 4.0$, the local axes are aligned parallel or only slightly misaligned. If $G < 4.0$, significant exchange coupling is present and the misalignment is appreciable.

Table 3. IR spectral data of ligand and their metal complexes.

	Frequency (cm^{-1})					
Compounds	υ(N–N)	υ(P–H)	υ(C=N)	υ(M–N)	υ(M–Cl)	$[\mathrm{PF}_6]$
$\mathrm{C}_{15}\mathrm{H}_{26}\mathrm{N}_5\mathrm{P}$	1286	2285	1636	–	–	–
$[\mathrm{Cu}(\mathrm{C}_{15}\mathrm{H}_{26}\mathrm{N}_5\mathrm{Cl}_2\mathrm{P})](\mathrm{PF}_6)_2$	1275	2240	1604	430	342	840
$[\mathrm{Co}(\mathrm{C}_{15}\mathrm{H}_{26}\mathrm{N}_5\mathrm{Cl}_2\mathrm{P})](\mathrm{PF}_6)_2$	1250	2212	1619	427	318	846
$[\mathrm{Ni}(\mathrm{C}_{15}\mathrm{H}_{26}\mathrm{N}_5\mathrm{Cl}_2\mathrm{P})](\mathrm{PF}_6)_2$	1248	2238	1588	442	328	838

The observed value for the exchange interaction parameter for the copper complex ($G > 4$) suggest that the local tetragonal axes are aligned parallel or slightly misaligned and the unpaired electron is present in $d_{x^2-y^2}$ orbital [29]. The spin orbit coupling constant, λ calculated using the relations, $g_{av} = 1/3[g_{\parallel} + 2g_{\perp}]$ and $g_{av} = 2(1 - 2\,\lambda/10D_q)$, is less free Cu(II) (−832), which also supports covalent character of M–L bond in the complex. The covalency parameter α^2 is calculated using the following equation:

$$\alpha^2_{\mathrm{Cu}} = A_{\parallel}/p + (g_{\parallel} - 2.0023) + 3/7(g - 2.0023) + 0.04$$

$\alpha^2 = 0.5$ indicates complete covalent bonding, while the value of $\alpha^2 = 1$ suggests complete ionic bonding. The observed value of α^2 of the complex is less than unity, which indicates that the complex has some covalent character [30].

3.5. *Electrochemical behavior*

Cyclic voltammetric studies of the copper complex show a well-defined redox process corresponding to formation of Cu(II)/Cu(I) couple at $E_{pa} = 0.543$ V and $E_{pc} = 0.260$ V. This couple is quasi-reversible with $\Delta E_p = 0.283$ V and the ratio of anodic to cathodic peak currents ($I_{pc}/I_{pa} \cong 1$) corresponding to a simple one-electron process. The peak current for the complex varies with scan rate and the ΔE_p ($E_{pa} - E_{pc}$) values are greater than 200 mV, indicating quasi-reversible reduction process and a chemical change occurring with electron transfer [31].

3.6. *NMR spectral data*

The ^{1}H NMR (300 MHz) spectrum for *bis*-(3,5-dimethyl-pyrazolyl-1-methyl)-(3-phosphanyl-propyl)-amine was recorded in $CDCl_3$. The spectrum of the free ligand showed a singlet at 2.79 ppm (12H) due to four methyl groups at 3,5-positions on the pyrazole rings. Pyrazole ring protons are a singlet at 5.84 ppm, a multiplet at 1.30–1.40 ppm is due to methylene protons (m, 4H, CH_2–CH_2), a triplet at 2.36, $J = 6.3$ Hz due to (N–CH_2–CH_2), a singlet at 4.8 ppm due to methylene proton (4H), 1.3 (2H, t, N–CH_2–CH_2–CH_2–PH_2, $J = 6.9$ Hz). The ^{31}P NMR high-field signal at −144.5 was attributed to the primary phosphine.

3.7. *Biological study*

The ligand and its metal complexes were evaluated for antibacterial activity against gram positive bacteria *Staphylococcus aureus*, *Bacillus subtilis*, gram negative bacteria *Escherichia coli* and fungi *Aspergillus niger* and *Aspergillus flavus* by disc diffusion. The test solutions were prepared in dichloromethane with nutrient agar used as culture medium. The zone of inhibition was measured in mm and the values of the investigated compounds are summarized in table 4.

From the observed result, metal complexes showed enhanced antimicrobial activity over the free ligand. Such increased activity of the metal complexes can be explained on the basis of Overton's concept [32] and chelation theory [33, 34].

The biological activities of the ligand and metal complexes are less than standard antifungal drug cephalosporin and antibacterial drug ciprofloxacin.

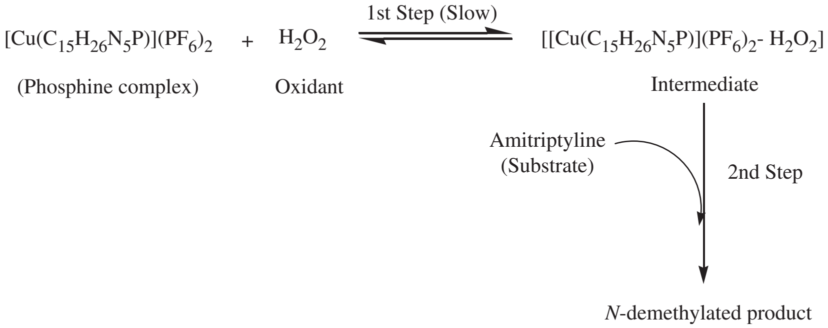
3.8. *Catalytic activity*

Hydrogen peroxide is an advantageous source of oxygen. Unfortunately, only a few catalysts have been discovered that allow for selective oxygenation of fine chemicals with this oxidant. Significant challenges still remain, e.g., the major problems in hydrogen peroxide catalytic oxidations are the stability of the catalyst involved with the reaction conditions.

Amitriptyline hydrochloride is metabolized by the oxidation of the side chain resulting in production of the secondary amine nortriptyline and *N*-oxide amitriptylin-oxide [34]. Catalytic oxidation of amitriptyline hydrochloride was performed in methanol owing to the good solubility of the complex and substrate in methanol. The catecholase activities of complexes have been studied by electronic spectroscopy by monitoring the appearance of the substituted *N*-demethylated product of amitriptyline. The oxidation of amitriptyline with hydrogen peroxide and phosphine complex proceeds to completion after 3 h with the production of a small amount of by-product and unreacted starting drug.

The amitriptyline hydrochloride was efficiently oxidized by this catalyst and oxidant and UV-visible overlays show loss of amitriptyline hydrochloride peak at 217 nm in the presence of hydrogen peroxide in 50% methanol [35]. The reaction was sluggish in the absence of catalyst. A plot of absorbance *versus* wavelength is shown in figure 1 and similar plots were obtained for the same reaction at the various concentrations of catalyst, hydrogen peroxide and amitriptyline.

The order of the reaction was found to be one respect to hydrogen peroxide and $Cu(C_{15}H_{26}N_5P)](PF_6)_2$. In contrast, the dependence on [amitriptyline hydrochloride] was approximately zero order. We propose the reaction mechanism which involves rate-determining conversion of the catalyst to an oxidized intermediate, which then transfers oxygen to amitriptyline hydrochloride in the fast step. The general mechanism shown below is widely accepted [36].



The phosphine complex is an effective catalyst for hydrogen peroxide (10^{-4} M) in the presence of 0.001 M drug. In large amount of hydrogen peroxide and phosphine complex, oxidation of tricyclic amitriptyline proceeds smoothly without formation of any byproduct and with only a small amount of remaining starting drug. The catalytic activity studies of the present complexes reveal that compared to other complexes,

Table 4. Antibacterial activity data of the ligand and their metal complexes (zone of inhibition in mm).

	Zone of inhibition (mm)				
Compounds	*S. tyohi*	*S. aureus*	*E. coli*	*A. niger*	*A. flavus*
$C_{15}H_{26}N_5P$	14	13	14	15	14
$[Cu(C_{15}H_{26}N_5Cl_2P)](PF_6)_2$	18	19	17	19	18
$[Co(C_{15}H_{26}N_5Cl_2P)](PF_6)_2$	19	18	18	20	17
$[Ni(C_{15}H_{26}N_5Cl_2P)](PF_6)_2$	19	20	19	18	19
Cephalosporin	22	24	22	23	24
Ciprofloxacin	21	24	21	21	24

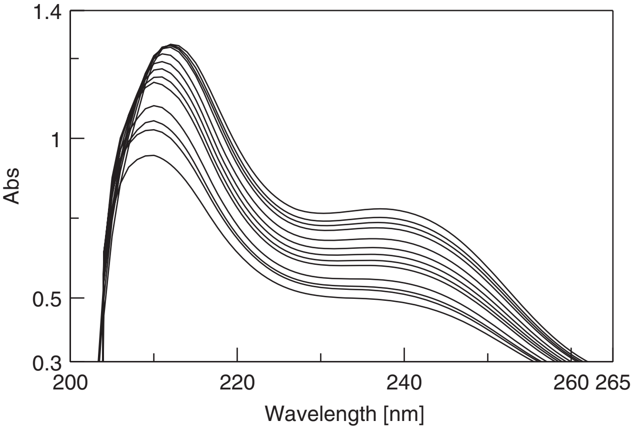


Figure 1. Plot of absorption *vs.* wavelength of amitriptyline hydrochloride by addition of H_2O_2 and $[Cu(C_{15}H_{26}N_5P)](PF_6)_2$.

copper complexes have significant catalytic activity for oxidation of amitriptyline hydrochloride to its corresponding *N*-demethylated amitriptyline oxide.

4. Conclusion

Complexes of *bis*-(3,5-dimethyl-pyrazolyl-1-methyl)-(3-phosphanyl-propyl)-amine with Cu(II), Co(II), and Ni(II) were characterized by various spectroscopic techniques, elemental analysis and magnetic susceptibility measurements. The presence of hydrogen substituents on the P^{III} centers decrease their back bonding capabilities, concomitantly increasing the electron densities of the primary phosphine bound metals. Increase in the electron density of metals leads to efficient oxidative addition processes in metal catalyzed organic transformation [4]. Therefore, transition metal complexes derived from *bis*-(3,5-dimethyl-pyrazolyl-1-methyl)-(3-phosphanyl-propyl)-amine ligand may play an important role in catalytic process.

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References

[1] R. Noyori. *Asymmetric Catalysis in Organic Synthesis*, John Wiley and Sons, New York (1994).
[2] L.H. Pignolet. *Homogeneous Catalysis with Metal Phosphine Complexes*, Plenum Press, New York (1983).
[3] B. Cornils, W.A. Herrman. *Aqueous-Phase Organometallic Catalysis*, Wiley-VCH, Weinhein (1998).
[4] C.A. Tolman. *Chem. Rev.*, **77**, 313 (1977).
[5] D.G. Gilheany. In *The Chemistry of Organophosphorus Compounds*, F.R. Hartley (Ed.), John Wiley and Sons, Chichester (1990).
[6] P.C.J. Kamer, P.W.N.M. Van Leeuwen, J.N.H. Reek. *Acc. Chem. Res.*, **34**, 895 (2001).
[7] B.A. Arbuzov. *Pure Appl. Chem.*, **9**, 307 (1964).
[8] K.V. Katti, H. Gali, D.E. Berning, C.J. Smith. *Acc. Chem. Res.*, **32**, 9 (1999).
[9] K.V. Katti. *Curr. Sci.*, **70**, 219 (1996); Chem. Abstract, **124**, 305 (1996).
[10] S.A. Reiter, B. Assmann, S.D. Nogai, N.W. Motzel, H. Schmidbaur. *Helv. Chim. Acta*, **85**, 1140 (2002).
[11] M. Brynda, M. Geoffroy, G. Bernardinelli. *Chem. Commun.*, 961 (1999).
[12] N.J. Goodwin, W. Henderson, B.K. Nicholson, J. Fawcett, D.R. Russell. *J. Chem. Soc., Dalton Trans.*, 1785 (1999).
[13] G. Ramakrishnan, A. Jouaiti, M. Geoffroy, G. Bernardinelli. *J. Phys. Chem.*, **100**, 10861 (1996).
[14] K. Raghuraman, N. Pillarsetty, W.A. Volkert, C.L. Barnes, S. Jurission, K.V. Katti. *J. Am. Chem. Soc.*, **124**, 7276 (2002).
[15] L. Heuer, D. Schomborg, R. Schmutzler. *Chem. Ber.*, **122**, 1473 (1989).
[16] R.A. Bartlett, M.M. Olmstead, P.P. Power, G.A. Sigel. *Inorg. Chem.*, **26**, 1941 (1987).
[17] H. Gali, S.R. Karra, V.S. Reddy, K.V. Katti. *Angew Chem. Int. Ed.*, **38**, 2020 (1999).
[18] K.R. Prabhu, N. Pillarsetty, H. Gali, K.V. Katti. *J. Am. Chem. Soc.*, **122**, 1554 (2000).
[19] N. Pillarsetty, K. Raghuraman, C.L. Barnes, K.V. Katti. *J. Am. Chem. Soc.*, **127**, 331 (2005).
[20] D.J. Brauer, J. Fischer, S. Kuchen, K.P. Langhans, O.Z. Stelzer. *Naturforsch., Teil B*, **49**, 1511 (1994).
[21] A. Koji, K. Matsfuji, M. Ohba, H. Okawa. *Inorg. Chem.*, **41**, 4461 (2002).
[22] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, 2nd Edn, Elsevier, Amsterdam (1984).
[23] R.L. Duta, A. Syamal. *Elements of Magnetochemistry*, 2nd Edn, Elsevier, New Delhi (1992).
[24] G.M. Sashidhara, T.R. Goudar. *J. Indian Chem. Soc.*, **78**, 360 (2001).
[25] A.A. Khandar, Z. Rezvani. *Polyhedron*, **18**, 129 (1998).
[26] J.Y. Shen, C. Slugove, P. Wiede, K. Mereiter, R. Schmid, K. Kirchner. *Inorg. Chim. Acta*, **268**, 69 (1998).
[27] D. Kivelson, R. Neiman. *J. Chem. Phys.*, **35**, 149 (1961).
[28] D.N. Satyanarayana. *Electronic Absorption Spectroscopy and Related Techniques*, Universities Press, Hyderabad (2001).
[29] B.J. Hathaway, D.E. Billing. *Coord. Chem. Rev.*, **6**, 143 (1970).
[30] S.M. Annigeri, A.D. Naik, U.B. Gangadharmath, V.K. Revankar, V.B. Mahale. *Transit. Metal Chem.*, **27**, 316 (2002).
[31] K.G. Dutton, G.D. Fallon, K.S. Murray. *Inorg. Chem.*, **27**, 34 (1988).
[32] P. Knopp, K. Weighardt, B. Nuber, J. Weiss, W.S. Sheldrick. *Inorg. Chem.*, **29**, 363 (1990).
[33] Y. Anjaneyalu, R.P. Rao. *Synth. React. Inorg. Met.-Org. Chem.*, **26**, 257 (1986).
[34] L. Mishra, V.K. Singh. *Indian J. Chem.*, **32A**, 446 (1993).
[35] A.M. Moreno-Fern, M.D. Cordero, M. Miguel, M.D. Delgado-Rufino, J.A. Sanchez-Alcazar, P. Navasb. *Toxicology*, **243**, 51 (2008).
[36] P. Prakash, L.J. Francisca Marcy. *Oxidation Commun.*, **28**, 983 (2005).