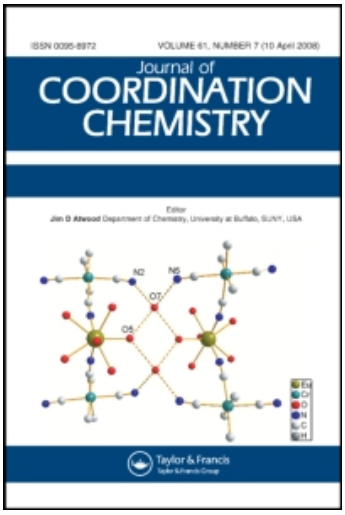

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Catalytic and biological activity of transition metal complexes of salicylaldiminopropylphosphine

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Catalytic and biological activity of transition metal complexes of salicylaldiminopropylphosphine

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Primary phosphine complexes of transition metals have been synthesized from salicylaldiminopropylphosphine. The complexes were characterized by elemental analysis, infrared, electronic, ^{1}H NMR, ^{31}P NMR spectra, magnetic susceptibility, and conductivity measurements. The studies indicate square planar geometry for copper, cobalt, and nickel complexes. The EPR spectra of copper complex in acetonitrile at 300 and 77 K were recorded. The biological activities of the ligand and metal complexes have been studied on microorganisms such as *Salmonella typhi*, *Staphylococcus aureus*, *Escherichia coli*, *Aspergillus niger*, and *Aspergillus flavus* by the well-diffusion method. The zone of inhibition values were measured at 37°C for 24 h. The electrochemical behavior of copper complexes was studied by cyclic voltammetry. The copper(II) complex oxidizes cinnamaldehyde using hydrogen peroxide as oxidant.

Keywords: 3-Aminopropylphosphine; Salicylaldiminopropylphosphine; Metal complexes; Catalytic activity; Biological activity

1. Introduction

Research in phosphorus chemistry has produced myriad organic and inorganic compounds [1–4]. Phosphorus–carbon compounds are versatile ligands for catalytically useful transition metal compounds, chemical precursors, or synthons in the development of antimicrobial, antibacterial agents, and development of broad spectrum herbicides [5]. Primary phosphine ligands are highly air sensitive; many derivatives, particularly those containing lower alkyl groups, are pyrophoric. Only a very small number of primary phosphines are known to be air stable [6]. Here we describe the synthesis of air stable primary phosphine ligands by condensation of salicylaldehyde with 3-aminopropyl phosphine and report their metal complexes in the catalytic oxidation of cinnamaldehyde.

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2. Experimental

All reagents and solvents were purchased from commercial suppliers and used without purification. All reactions were carried out under nitrogen. Elemental analyses were performed at CDRI, Lucknow. UV-Vis spectra of the ligand and metal complexes were recorded in dichloromethane using a JASCO V-530 spectrophotometer. IR spectra were recorded on a Shimadzu spectrophotometer (Model FTIR-8400S) and 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 0.1 M Ag/AgCl electrode, Pt wire auxiliary electrode, and glassy carbon working electrode with TBAP as supporting electrolyte. ^{1}H 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 solvent and 85% H_3PO_4 as the external reference, at IISc, Bangalore. ESR spectra were recorded in solid state at 300 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 $\mu_{\text{eff}} = 2.228(\chi_M T)^{1/2}$, where χ_M is the corrected molar susceptibility. Molar conductance of the complexes was measured in methanol at room temperature using a Systronic conductivity bridge type (OSWAL).

2.1. *Preparation of salicylaldiminopropylphosphine ($C_{10}H_{14}ONP$) (1)*

To 2.4 mL (20 mmol) of salicylaldehyde dissolved in 20 mL ethanol a total of 1.819 g (20 mmol) of 3-aminopropylphosphine in 15 mL ethanol was added. This reaction mixture was refluxed for 3 h, then concentrated to 5–10 mL and cooled in ice giving yellow solid which was filtered and dried under vacuum, m.p. 145°C; Elemental analysis (Found: C, 61.25; H, 7.35; N, 7.26; $C_{10}H_{14}NOP$; Calculated: C, 61.56; H, 7.16; N, 7.16). ν_{max} (KBr) cm^{-1} 3383 (O–H), 1642 (C=N), 1273 (P–H); ^{1}H NMR δ (300 MHz; $CDCl_3$), 6.7–7.5 δ (4H, m, aromatic ring proton), 8.13 δ (1H, s, CH) due to Ar–H proton, 1.7 δ (2H, m, CH_2–C**H**$_2$–CH_2), 3.5 δ (2H, t, N–C**H**$_2$–CH_2–CH_2, $J = 7.5$ Hz), 1.3 δ (2H, t, CH_2–CH_2–CH_2–PH_2, $J = 7.2$ Hz); ^{31}P NMR shows signal (161 MHz; $CHCl_3$) at −138.7 ppm due to the primary phosphine moiety.

2.2. *Preparation of metal complexes [$C_{10}H_{14}NOPMCl(PF_6)_2$] (M = Cu(II), Co(II), and Ni(II))*

To 0.390 g (2 mmol) of salicylaldiminopropylphosphine dissolved in dichloromethane a total of 2 mmol of metal chloride (MCl_2, M = Cu(II), Co(II), and Ni(II)) was added. To this mixture, 0.334 g (2 mmol) of sodium hexafluorophosphate and a small amount of triethylamine was added. This reaction mixture was stirred for 3 h. Reducing the volume followed by addition of petroleum ether, precipitated metal complexes which were filtered, washed with ether, and dried under vacuum.

2.3. *Biological activity*

The *in vitro* antimicrobial activity of the compounds was tested against *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli*, and fungi like *Aspergillus niger* and *Aspergillus*

flavus by the well-diffusion method. Stock solutions (10^{-3} M) were prepared by dissolving the compounds in acetonitrile. In a typical procedure, a well was made on the agar medium inoculated with microorganisms. The well was filled with the test solution using a micropipette and the plate was incubated at 35°C for 24 h. During this period, the test solution diffused and the effect on growth of the inoculated microorganisms was measured.

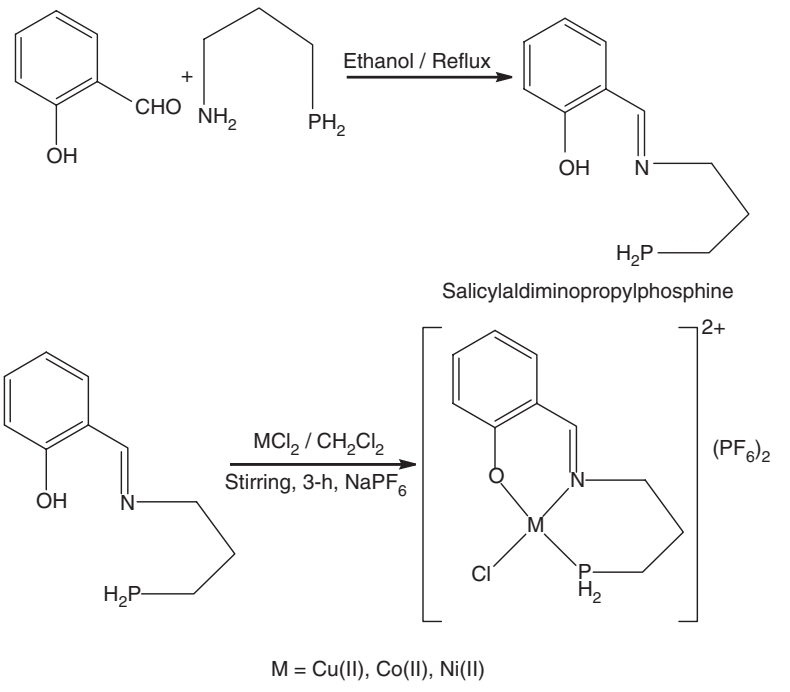
2.4. *Catalytic activity*

Since catalytic reactions were not significantly affected by molecular oxygen, they have been performed under air. The quartz cuvette was first charged with 1775 μL of methanol. Then 100 μL of methanol solution of metal catalyst (1.88×10^{-4} mol dm^{-3} stock) to give 9.4×10^{-6} mol dm^{-3} in the cell and 25 μL of methanol solution of cinnamaldehyde (0.1 mol dm^{-3} stock) to give a concentration in cell 1.25×10^{-3} mol dm^{-3} were injected into the cell and allowed to come to equilibrium for 5 min. The reaction was initiated by injecting the oxidant, 100 μL of 0.05 mol dm^{-3} stock in methanol to give 2.5×10^{-3} mol dm^{-3} in the cell. The absorbance at 250 nm was measured as a function of time. Similar kinetic analysis was made by varying [oxidant] and [catalyst] with the proper ratio of oxidant, catalyst, and solvent as given in "Supplementary material".

3. Results and discussion

The ligand was prepared by condensation of 3-aminopropylphosphine with salicylaldehyde in a 1 : 1 molar ratio. The synthon 3-aminopropylphosphine was synthesized through the literature method and stored under nitrogen [7–9]. Primary phosphines are usually air-sensitive liquids. Most crystal structures with RPH_2 have therefore been determined on molecules where the phosphorus is coordinated to a metal [10–13]. The crystal structure of free primary phosphines could be obtained in only a very limited number of cases: (i) when the phosphorus is bound to a bulky protective aryl group $(Bu^t_3C_6H_2)^2$, to an iron dicyclopentadienyl group [14], or to a triptycyl moiety [15]; (ii) after dimerization of anthracenephosphine [16]; (iii) after N-quaternization of aminoalkylphosphines [17]. Recent results [18] indicated that free primary monophosphines containing bulky groups sterically crowd the phosphorus rendering stability to P–H bonds [19–22]. The reason for the unusual oxidative stability of primary phosphine from the earlier work of Gali *et al.* [23], Prabhu *et al.* [24], Pillarsetty *et al.* [25], and Brauer *et al.* [17] suggest that electronegative heteroatom such as nitrogen or sulfur, two or three carbons away from the phosphorus, have negative hyper conjugative electronic influence on the P^{III} center and thus render the primary phosphine oxidatively stable [23, 25]. We have taken advantage of this to synthesize a primary phosphine, which contains a hetero nitrogen. We report in the following text the synthesis and structure of the remarkably air-stable primary phosphine. The synthesis of salicylaldiminopropylphosphine is shown in scheme 1.

The elemental analysis data of salicylaldiminopropylphosphine and metal complexes are presented in table 1. The values are in agreement with the general formula MLX (X = Cl) for metal : ligand ratio 1 : 1. The metal complexes were dissolved in acetonitrile



Scheme 1. Synthesis of ligand and complexes.

Table 1. Elemental analysis data of the ligands and metal complexes.

	Analysis found (Calcd) (%)				
Compound	M	C	H	N	m.p. (°C)
$C_{10}H_{14}NOP$ (**1**)	–	61.35	7.12	7.03	145
	–	(61.53)	(7.23)	(7.18)	
$[C_{10}H_{13}NOClCuP](PF_6)_2$ (**2**)	10.83	20.38	2.03	2.19	275
		(10.90)	(20.60)	(2.25)	(2.40)
$[C_{10}H_{13}NOClCoP](PF_6)_2$ (**3**)	10.01	20.59	2.11	2.24	292
	(10.19)	(20.76)	(2.27)	(2.42)	
$[C_{10}H_{13}NOClNiP](PF_6)_2$ (**4**)	10.02	20.55	2.04	2.21	284
	(10.15)	(20.77)	(2.27)	(2.41)	

and the molar conductivities of 10^{-3} M solutions at 25 ± 2°C were measured ($\Lambda_m = 9.35$–$18.27\ \Omega^{-1}mol^{-1}cm^2$) indicating non-electrolytes.

3.1. *IR spectra*

The IR spectrum of the free phosphine was compared with spectra of the complexes. Table 2 shows the characteristic IR bands of the ligand and its metal complexes. The IR spectrum of the ligand shows a stretching and bending band in the region 3450–3283 cm^{-1} assigned as υ(O–H), which is absent in the spectra of the complexes indicating deprotonation and involvement of the enol in chelation.

Table 2. Infrared spectral data of ligands and complexes.

Compound	Frequency (cm^{-1})						
	ν(O–H)	ν(P–H)	ν(C=N)	ν(M–N)	ν(M–O)	ν(M–Cl)	$[PF_6]^-$
1	3383	1273	1642	–	–	–	–
2	–	1228	1612	542	445	358	852
3	–	1234	1610	537	434	347	839
4	–	1240	1608	529	452	338	824

Table 3. Electronic spectral data and magnetic moments for ligand and complexes.

Compound	Frequency (cm^{-1})	Transition	Geometry	μ_{eff} (B.M.)
1	47,169	π–π^*	–	–
	39,370	n–π^*		
	30,864	Charge transfer		
2	24,691	$^2B_{1g} \rightarrow {}^2B_{2g}$	Square planar	1.72
	24,272	$^2B_{1g} \rightarrow {}^2E_g$		
	21,881	$^2B_{1g} \rightarrow {}^2A_{1g}$		
3	18,998	$^1A_{1g} \rightarrow {}^1B_{1g}$	Square planar	–
	35,037	INCT		
	25,822	INCT		
4	19,820	$^1A_{1g} \rightarrow {}^1A_{2g}$	Square planar	–
	15,938	$^1A_{1g} \rightarrow {}^1B_{1g}$		
	39,062			

The IR spectrum of the metal complexes showed υ(C=N) (for ligand at 1632 cm^{-1}) is shifted to lower frequency due to the coordination of azomethine nitrogen. The υ(P–H) bending vibration at 1273 cm^{-1} for ligand shifted lower for metal complexes suggesting that P is coordinated. In spectra of metal complexes new bands in the region 434–452 cm^{-1}, 358–338 cm^{-1}, and 529–542 cm^{-1} are assigned to υ(M–O), υ(M–Cl), and ν(M–N), respectively [26, 27]. The strong absorption at 824–852 cm^{-1} corresponds to $[PF_6]$ [28].

3.2. *Electronic spectra*

Electronic spectra of ligand, presented in table 3, show bands at 47,169, 39,370, and 30,864 cm^{-1}. The first band would be assigned to π–π^* transition within the aromatic ring. The second band would be due to n–π^* transition within the C=N. The absorption at 30,864 cm^{-1} was assigned to CT transition [29]. The copper complex exhibited absorptions at 24,691, 24,272, and 21,881 cm^{-1} assigned as $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2E_g$, and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions, respectively. These transitions were characteristic of square-planar geometry. The magnetic moment of the Cu(II) complex is 1.72 B.M., also consistent with square-planar configuration [30].

The cobalt(II) complex recorded in CH_2Cl_2 shows absorption at 18,998 cm^{-1}, tentatively assigned $^1A_{1g} \rightarrow {}^1B_{1g}$ transition. The magnetic moment of cobalt(II) complex is 3.54 B.M., additional evidence for square-planar geometry [31].

The nickel(II) complex exhibited two absorption bands at 19,820 and 15,938 cm^{-1}, tentatively assigned as $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transition, respectively. The magnetic moment of Ni(II) complex is zero, which indicates that the complex has square-planar structure [32, 33].

3.3. *Electrochemical behavior*

Electrochemical cyclic voltammetry measurements were carried out to probe the redox stability of the copper complex in solution. A conventional three-electrode system was used with a polished glassy carbon electrode as working electrode and a platinum wire counter electrode. The reference was an aqueous Ag/AgCl saturated electrode and tetrabutylammonium perchlorate was supporting electrolyte in acetonitrile. The solutions were freshly prepared before use and purged with N_2 saturated with solvent for *ca* 15 min prior to taking measurements in order to remove dissolved O_2. Voltammograms were recorded from 2.0 to −2.0 V.

The cyclic voltammogram of copper complex (Supplementary material) shows a well-defined redox process corresponding to the Cu(II)/Cu(I) couple at $E_{pa} = 0.49$ V and the associated cathodic peak at $E_{pc} = 0.41$ V. This couple is reversible with $\Delta E_p = 0.08$ V and the ratio of anodic to cathodic peak currents ($I_{pc}/I_{pa} \approx 1$) corresponding to a simple one-electron process [34, 35]. The complex also shows a quasi-reversible peak in the negative region, characteristic of the Cu(I)/Cu(0) couple at $E_{pc} = -0.84$ V with associated anodic peak at $E_{pa} = -0.48$ V.

3.4. *ESR spectra*

ESR spectra of copper(II) complex have been recorded at room temperature and liquid nitrogen temperature; bonding parameters are included in table 4. Four lines have been observed in the LNT spectra, which are unresolved at room temperature suggesting that a single copper is present and the complex is a monomer. A broadened spectrum was not observed, revealing that spin–spin interactions between copper centers are non-existent. G values, $G = (g_\parallel - 2.0023)/(g_\perp - 2.0023)$, are greater than four, indicating negligible interaction between copper centers [36] and the local tetragonal axes are aligned parallel or slightly misaligned with the unpaired electron in $d_{x^2-y^2}$ orbital [37]. Closeness of the g values to those reported for square-planar structure, $g_\parallel$ (2.253) > $g_\perp$(2.064) > g_e(2.0023), suggest square-planar geometry of the complex [38, 39]. The spin orbit coupling constant, λ(−457 nm) calculated using the relations, $g_{av} = 1/3(g_\parallel) + 2/3(g_\perp)$, is less than the free Cu(II) ion (−832 nm) indicating covalent character of M–L in the complex. The covalency parameter α^2 is calculated using the following equation

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

Table 4. ESR spectral data of copper(II) complex.

$g_{\parallel}$	$g_\perp$	g_{iso}	$A_{\parallel} \times 10^{-4}$ (cm^{-1})	$A_\perp \times 10^{-4}$ (cm^{-1})	$A_{iso} \times 10^{-4}$ (cm^{-1})	α^2	G
2.253	2.064	2.127	128	31.29	53	0.673	4.25

$\alpha^2 = 0.5$ indicates complete covalent bonding, while $\alpha^2 = 1$ suggests complete ionic bonding. The observed value of α^2 (0.673) indicates some covalent character in the ligand environment. g_{iso} and A_{iso} were calculated using the relation given in [40].

$$g_{iso} = 1/3\ (g_{\parallel} + 2g_{\perp}), \quad A_{iso} = 1/3\ (A_{\parallel} + 2A_{\perp}).$$

The g_{iso} is the most sensitive function for indicating covalency, being 2.3 or more for ionic compounds and less than 2.3 for covalent compounds; g_{iso} of 2.127 indicates covalent character of the metal–ligand bond.

3.5. *Biological study*

The ligand and its metal complexes were evaluated for antibacterial activity against gram positive bacteria *S. aureus* and *B. subtilis*, gram negative bacteria *E. coli* and fungi *A. niger* and *A. flavus* by the well-diffusion method. The test solutions were prepared in acetonitrile with nutrient agar used as culture medium. The zone of inhibition was measured in mm (table 5).

Metal complexes showed enhanced antimicrobial activity over free ligand due to greater lipophilic nature of the complexes [41–43].

Generally, it is suggested that the chelated complexes deactivate various cellular enzymes, which play a vital role in various metabolic pathways of these microorganisms. Other factors such as solubility, conductivity, and dipole moment, which are affected by the presence of metal ions, may also be possible reasons for increasing the biological activity of the metal complexes as compared to the corresponding ligand. The biological activities of the ligand and metal complexes were less than standard antifungal drug cephalosporin and antibacterial drug ciprofloxacin.

3.6. *Catalytic activity in the oxidation reaction by H_2O_2*

Hydrogen peroxide is an advantageous source of oxygen; unfortunately few catalysts allow for selective oxidation of fine chemicals with this oxidant. Significant challenges still remain, e.g. stability of the catalyst to the reaction conditions. Cinnamon bark is a spice that maintains blood sugar balancing effects. Cinnamaldehyde, the primary component of cinnamon bark, has potent antioxidant actions, protecting cells from oxidative damage and also is food flavoring, fungicide, pesticide, potential antibiotic, and demonstrating cytotoxic properties in some human tumor cells. Cinnamaldehyde is

Table 5. Antibacterial activity of the ligand and complexes.

	Zone of inhibition (mm)			
Compound	*S. typhi*	*S. aureus*	*E. coli*	*B. subtilis*
Ligand	13	11	14	10
$[CuL_2]$	18	17	18	16
$[CoL_2]$	16	14	16	19
$[NiL_2(H_2O)_2]$	15	17	19	17
Ciprofloxacin	23	24	22	23

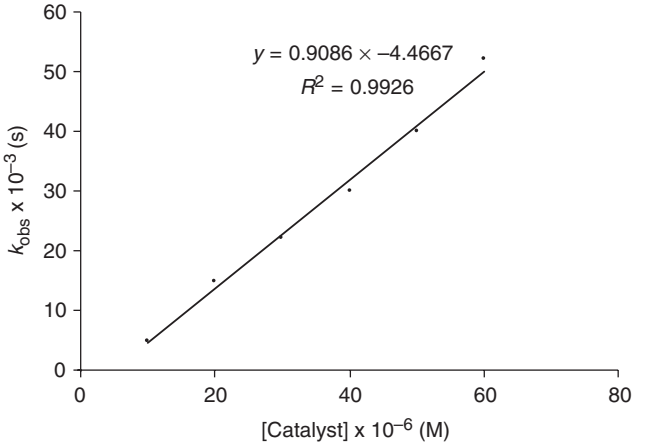


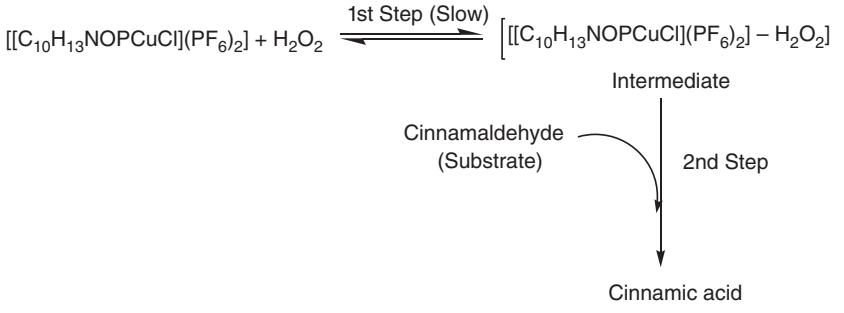
Figure 1. Reaction order with respect to (**2**) on catalyzed oxidation of cinnamaldehyde in methanol at 25°C.

metabolized to cinnamic acid after intravenous application with half life of 1.7 h. The majority of the cinnamaldehyde administered is excreted in urine as hippuric acid. Due to its ready biodegradation and low potential for bioaccumulation, effects on living organisms are not to be expected. The skin absorption and metabolism of cinnamaldehyde will play an important role in oxidoreductase enzymes such as alcohol dehydrogenase. Cinnamaldehyde could be a potential drug for treatment of Chagas disease, especially because the activity against the amastigote stage and the role of this stage in the pathogenesis of the disease [44]. Hence, we examine the catalytic activity of **2** with *Cinnamomum cassia* bark methanolic extract: 3-phenyl-2-propenal (cinnamaldehyde).

It is evident from the work of Cho *et al.* that H_2O_2 does not oxidize phosphine [45]. Cinnamaldehyde was efficiently oxidized by **2** and H_2O_2 as oxidant; UV-Vis overlays showed loss of cinnamaldehyde peak at 250 nm in the presence of hydrogen peroxide in methanol. The reaction was sluggish in the absence of catalyst. Reaction orders have been determined by monitoring the disappearance of cinnamaldehyde at 250 nm in the reaction catalyzed by our metal complex at the early stage of oxidation reaction where the relationship between the aldehyde conversions *versus* time was linear. We determined the dependence of reaction rate on various concentrations of cinnamaldehyde, metal complex catalyst, and oxidant. All reagent concentrations used were independent of cinnamaldehyde. Rate constants are presented in "Supplementary material". Duplicate kinetic runs showed that the rate constants are reproducible to within ±3%. The rate of the reaction was found to be independent of the initial concentration of the oxidant indicating zero order dependence on [oxidant]. The rate increased steadily with increase in [metal complex catalyst]. A linear plot of k_{obs} *versus* [metal complex] with the slope of unity (figure 1) indicates first order dependence of the rate of the reaction on [metal complex].

The kinetic results of this system of cinnamaldehyde by hydrogen peroxide and metal complex allow us to give a rate law for the metal complex catalyzed oxidation of cinnamaldehyde by hydrogen peroxide as,

$$\frac{-\mathrm{d[cinnamaldehyde]}}{\mathrm{dt}} = k_{obs}\,[\text{metal complex}]$$



Scheme 2. General mechanism of catalytic oxidation of cinnamaldehyde by using copper(II) complex.

consistent with the mechanism of metalloporphyrin complex-catalyzed oxidation [46] as shown in scheme 2, with the rate-determining conversion of the catalyst to an oxidized intermediate, which then transfers oxygen to the substrate, cinnamaldehyde in the fast step [45, 47].

4. Conclusion

Complexes **2**, **3**, and **4** are square planar from spectral and analytical data and show enhanced antimicrobial activity compared to the free ligand. The copper(II) complex is an efficient catalyst in oxidation of cinnamaldehyde. This type of complex can be further investigated in metabolic study of various drug molecules.

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