



## Synthesis and phosphatase activity of a Cobalt(II) phenanthroline complex

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**Abstract.** A mononuclear cobalt(II) complex, [Co(phen)<sub>2</sub>Cl<sub>2</sub>], (phen = 1,10-phenanthroline) has been synthesized and structurally characterized by different spectroscopic methods including single crystal X-ray structural study. X-ray crystal structural analysis revealed that the cobalt(II) complex crystallizes in a monoclinic system with *C2/c* space group and exists in cis-configuration in its crystalline state. Room temperature magnetic measurement accounts for 3e paramagnetism and indicates high spin cobalt(II) in the solid state. The cobalt(II) complex has been evaluated as a functional model for phosphatase enzyme by using 4-nitrophenylphosphate (PNPP) as a standard substrate in aqueous DMF medium. This mononuclear cobalt(II) complex exhibits good hydrolytic phosphoester cleavage efficiency with *k*<sub>cat</sub> value of 3.78 × 10<sup>2</sup>h<sup>-1</sup>.

**Keywords.** Cobalt(II); 1,10-phenanthroline; crystal structure; supramolecular interactions; phosphatase activity.

### 1. Introduction

Designed coordination molecules with an ability to mimic the active sites of several bio-enzymes in an effective manner can lead to efficient bio-inspired catalysts having laboratory and industrial uses.<sup>1–3</sup> Cobalt is an essential bio-element and found in cobalamin and in a few other metallo-proteins.<sup>4</sup> Cobalamin is necessary for the formation of myelin, an insulating layer found around nerves, supporting the production of red blood cell, for the metabolism of fats and carbohydrates, and in the synthesis of proteins.<sup>4</sup> Cobalt complexes containing polypyridyl ligand have several appealing structural and chemical properties in biological systems, as therapeutic agents and for drug design.<sup>5,6</sup> Cobalt(II) complexes are interesting for their capability to bind dioxygen reversibly<sup>7–9</sup> and for their catalytic

applicability in different oxidation reactions,<sup>10–13</sup> in particular for the oxidation of phenols, alcohols, flavonoids, nitroalkanes, hydrazines or olefins.<sup>14–16</sup> In addition, cobalt complexes have gained importance because of their application as potential hypoxia-activated prodrugs.<sup>17</sup> Phosphoesterase enzyme in biological systems plays a vital role in the functioning DNA fragmentation, RNA replication, bone metabolism, chemotherapy and bio-remediation of organophosphate pesticides.<sup>18</sup> The active site of the phosphoesterase enzyme typically consists of zinc ion and the metal centre is surrounded by N linkages from histidine ligands or O coordination from an aspartate, and often with bridging hydroxide ion.<sup>19</sup> Although a similar complex has been reported by Hazell *et al.*,<sup>20</sup> we have produced this Co(II) complex following a different methodology. In our previous work, we have also investigated

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the biological activity of  $[\text{Co}(\text{phen})_2\text{Cl}_2](\text{NO}_3)_x \cdot x\text{H}_2\text{O}$  including anticancer activity.<sup>5b</sup> Herein, we report an octahedral mononuclear cobalt(II) phenanthroline complex,  $[\text{Co}(\text{phen})_2\text{Cl}_2]$  (**1**) with X-ray crystal structure and its hydrolytic cleavage ability of phosphoester bond towards sodium salt of 4-nitrophenylphosphate (pNPP) with good turnover number,  $k_{\text{cat}} = 3.78 \times 10^2 \text{h}^{-1}$  in aqueous DMF medium.

## 2. Experimental

### 2.1 Materials

High purity 1,10-phenanthroline (Lancaster, UK), cobalt(II) chloride hexahydrate, sodium azide, and glacial acetic acid (E. Merck, India) were purchased and used as received. All the other reagents and solvents are of Analytical grade (A.R. grade) and were purchased from commercial sources and used as received.

### 2.2 Synthesis of $[\text{Co}(\text{phen})_2\text{Cl}_2](\text{I})$

$\text{NaN}_3$  solution (0.76 g, 1 mM) was added drop by drop to a solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.237 g, 1 mM) in the same solvent (20 mL) followed by the addition of 1,10-phenanthroline (0.360 g, 2 mmol) in  $\text{H}_2\text{O}$  (10 mL) and the resulting solution was kept in reflux for 3 h. The solution was filtered and kept in air for slow evaporation. After 12–15 days the fine microcrystalline product was separated by decantation, washed with n-hexane and dried *in vacuo* over silica gel indicator. Yield: 0.167 g (~71%). Anal. Calc. for  $\text{C}_{20}\text{H}_{20}\text{N}_4\text{Cl}_2\text{Co}$ : C 58.80, H 3.29, N 11.43%. Found: C 58.84, H 3.25, N 11.49%. Selected IR bands (KBr pellet,  $\text{cm}^{-1}$ ): 1636(s), 1605(s), UV–Vis ( $\lambda$ , nm,  $10^{-4}$  M, 1 cm optical pathlength, abs, aqueous medium): 240–270 (2.30), 353 (0.4384), 530–600 (0.0145); ESI-MS ( $\text{H}_2\text{O}$ ): m/z, 438.68 (Calc. 438.08).

### 2.3 Physical measurements

Infrared spectrum (KBr) was recorded with a FTIR-8400S SHIMADZU spectrophotometer in the range 400–3600  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum in  $\text{DMSO}-d_6$  was obtained on a Bruker Avance 300 MHz spectrometer at 25°C and was recorded at 299.948 MHz. Ground state absorption was measured with a JASCO V-730 UV–Vis spectrophotometer. Elemental analyses were performed on a Perkin Elmer 2400 CHN microanalyser. Electrospray ionization (ESI) mass spectrum was recorded using a Q-tof-micro quadrupole mass spectrometer. A Gouy balance was used to determine the magnetic susceptibility of the powdered sample, employing  $\text{Hg}(\text{II})$  tetrathiocyanatocobaltate(II) as a calibrant. Diamagnetic corrections were made from the Pascal's constants. The Electron Paramagnetic Resonance (EPR) spectrum was recorded on a Bruker EMX-X band spectrometer (Model: EMX).

### 2.4 Crystal structure determination and refinement

Single crystal X-ray diffraction data were collected using a Rigaku XtaLABmini diffractometer equipped with Mercury375R ( $2 \times 2$  bin mode) CCD detector. The data were collected with graphite monochromated Mo- $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{Å}$ ) at 100.0(2) K using  $\omega$  scans. The data were reduced using Crystal Clear suite, and the space group determination was done using Olex<sup>2</sup>. The structure was resolved by direct method and refined by full-matrix least-squares procedures using the SHELXL-97 software package using OLEX<sup>2</sup> suite.<sup>21,22</sup>

### 2.5 Phosphatase activity of $[\text{Co}(\text{phen})_2\text{Cl}_2](\text{I})$

To examine the nature of hydrolytic cleavage of phosphoester bond by  $[\text{Co}(\text{phen})_2\text{Cl}_2]$  in aqueous DMF medium we have used disodium salt of (4-nitrophenyl)phosphate (PNPP) as a standard substrate following a previously reported procedure.<sup>23</sup> The hydrolysis rate of PNPP in the presence of the cobalt complex was measured by an initial rate method keeping fixed the incremental band intensity in absorption at 416 nm due to the released p-nitrophenolate ion in aqueous DMF at 25°C. For the wavelength scan, the spectrum was recorded by mixing a solution containing  $1 \times 10^{-4}$  M PNPP and  $1 \times 10^{-2}$  M cobalt(II) complex for 2 h.

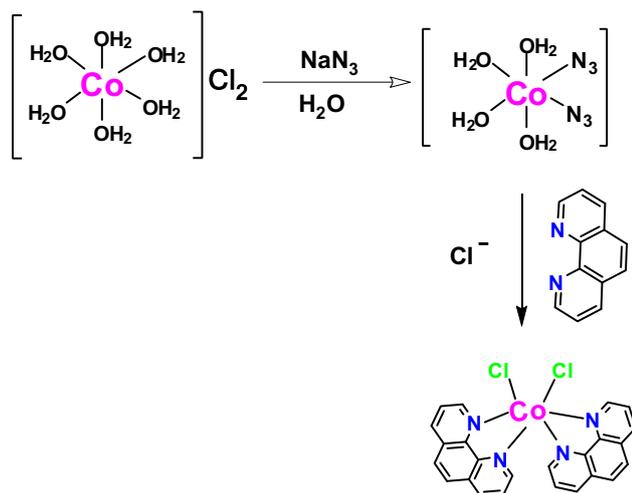
Kinetics experiments of the phosphoester cleavage of PNPP were performed by monitoring the growth of the 4-nitrophenolate band at 416 nm as a function of time under the condition of excess substrate in presence of Co(II) complex, keeping the other parameters constant. Kinetic experiment was performed with **1** (at a constant concentration of  $1 \times 10^{-4}$  M) and PNPP (varying the concentration from  $1 \times 10^{-3}$  to  $1 \times 10^{-2}$  M) in aqueous DMF using UV–Vis spectrophotometer. The visible absorption increase was recorded for a total period of 2 h at 9 min intervals. All the measurements were performed in triplicate.

## 3. Results and Discussion

### 3.1 Synthesis and proposed mechanism for the preparation of the cobalt(II) complex

$[\text{Co}(\text{phen})_2\text{Cl}_2]$  was prepared by slow addition of aqueous solution of  $\text{NaN}_3$  to  $\text{CoCl}_2$  in the same solvent followed by the addition of aqueous solution of phenanthroline. Our aim was to prepare a cobalt compound containing phenanthroline and azide ligands by such reaction methodology. But we produced a cobalt(II) complex containing phenanthroline ligand and it is poorly soluble in all the common solvents like methanol, acetonitrile, water, etc.

To investigate the mechanistic pathway behind the formation of such Co(II) complex as the major product, we observed that  $\text{NaN}_3$  helped to create a reducing

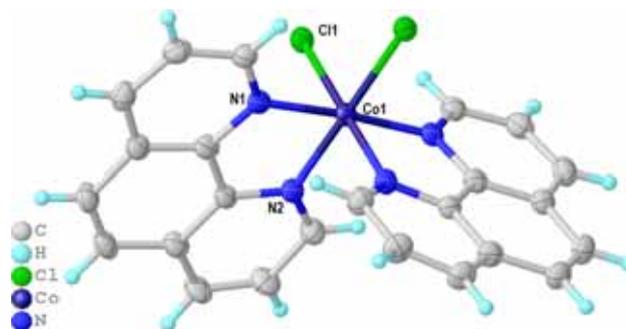


**Scheme 1.** Proposed mechanism for synthesis of Co(II) complex.

environment in the reaction mixture.<sup>24</sup> At the primary stage of the reaction the pale pink solution of the Co(II) salt turned instantly brown during the addition of azide and indicated the incorporation of the azide ions into the coordination sphere of Co(II) centre with the displacement of chloride ions. At refluxing condition in presence of trace amount of glacial acetic acid, Co(II) centre kept itself stabilized in its lower oxidation state and complexation occurred with 1,10-phenanthroline ( $\pi$ -acidic ligand), which is known as a good stabilizer<sup>25</sup> for metal ions having lower oxidation states. The chloride ions which get displaced at the primary stage may now act as a better nucleophile than water molecule and forms a *cis*-dichloro bis(phenanthroline) cobalt(II) complex. Controlled experiments under the same conditions in the absence of  $\text{NaN}_3$  revealed that for successful production of this cobalt(II)-phen complex, sodium azide is essential (Scheme 1). We used this reaction methodology previously in the preparation of an oxido-bridged diiron(II)-phenanthroline compound.<sup>24</sup>

### 3.2 Crystal structure

The molecular structure of  $[\text{Co}(\text{phen})_2\text{Cl}_2]$  (**1**) is shown in Figure 1, while the structural refinement parameters are given in Table 1. Selected bond lengths and angles are listed in Table S1 (in Supplementary Information). According to the X-ray data, the complex crystallizes in the monoclinic system with  $C2/c$  space group. The coordination geometry around the Co(II) centre is best described as a distorted octahedron with a  $\text{CoN}_4\text{Cl}_2$  coordination core formed by four nitrogen atoms of two bidentate phenanthroline ligands and two chlorine atoms (Figure 1). The  $\text{Cl}(2)\text{--Co}(1)\text{--Cl}(2^*)$

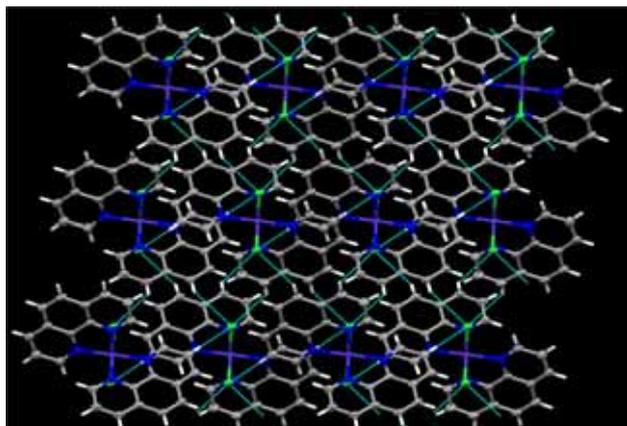


**Figure 1.** Thermal ellipsoid (30%) plot of the cation of  $[\text{Co}(\text{phen})_2\text{Cl}_2]$  (**1**).

**Table 1.** Crystallographic data of  $[\text{Co}(\text{phen})_2\text{Cl}_2]$  (**1**).

Parameters	Co(II) compound
Empirical formula	$\text{C}_{24}\text{H}_{16}\text{N}_4\text{Cl}_2\text{Co}$
Formula weight	490.24
Temperature (K)	100.0(2)
Crystal system	Monoclinic
Space group	$C2/c$
<i>a</i> (Å)	15.3582(7)
<i>b</i> (Å)	13.0120(6)
<i>c</i> (Å)	13.1966(7)
Volume (Å <sup>3</sup> )	2582.7(2)
<i>Z</i>	4
$\rho$ (gcm <sup>-3</sup> )	1.261
$\mu$ (mm <sup>-1</sup> )	0.887
<i>F</i> (000)	996
$\theta$ ranges (°)	2.7–32.8
<i>R</i> <sub>int</sub>	0.038
<i>R</i> (reflections)	15618
w <i>R</i> <sup>2</sup> (reflections)	4565
Final <i>R</i> indices	0.0593, 0.1862
Largest peak and hole (eÅ <sup>-3</sup> )	1.54, -0.74

angle (91.61°) indicates the *cis* conformation of the structure. Though there is a possibility to exist in *cis*- and *trans*-form of the Co-phen complex, but lower solubility of the *cis*- conformation accounts for the primary isolation of *cis*- $[\text{Co}(\text{phen})_2\text{Cl}_2]$  in the form of single crystals. In solid state, adjacent complex units,  $[\text{Co}(\text{phen})_2\text{Cl}_2]$  are interlinked to form an interpenetrating 3D supramolecular architecture through a number of  $\text{C--H}\cdots\text{Cl}$  intermolecular hydrogen bonds (Figure 2). In the construction of 3D superstructure through strong intermolecular H-bonding interactions ( $\text{C}2\text{--H}2\cdots\text{Cl}1$ ,  $\text{C}6\text{--H}6\cdots\text{Cl}1$ ,  $\text{C}8\text{--H}8\cdots\text{Cl}1$ ), hydrogen atoms (H1, H6, H8, H10) attached to aromatic carbon atoms act as acceptors while chlorine atom (Cl1) coordinated to cobalt(II) centre behave as donor centre. The values of  $\text{H}\cdots\text{Cl}$  supramolecular interactions remain very close to  $\sim 2.8\text{Å}$  which are weak but acceptable in

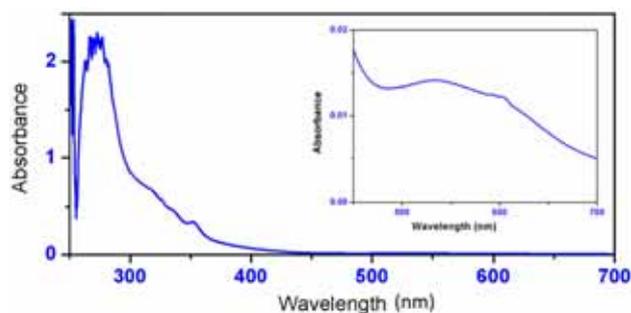


**Figure 2.** Formation of 3D crystalline architecture through intermolecular H...Cl hydrogen bonds in  $[\text{Co}(\text{phen})_2\text{Cl}_2]$  (**1**).

scientific literature<sup>5b, 6a</sup> on the perspective of H...Cl interactions. The details of C–H...Cl intermolecular hydrogen bonds are given in Table S2 (in Supplementary Information) (Figure 2).

### 3.3 Electronic spin and solution properties

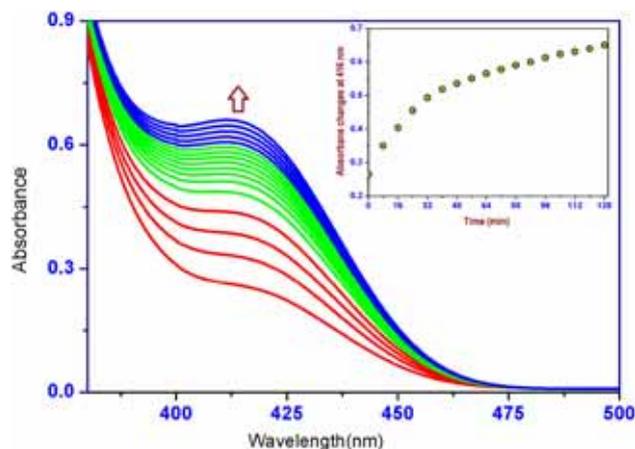
Cobalt(II) complexes exhibit interesting magnetic susceptibility at room temperature and low temperature, and often displays spin-state transition phenomenon.<sup>26–30</sup> We find room temperature magnetic susceptibility value,  $\mu_{\text{eff}} = 4.78 \mu\text{B}$  for this cobalt(II) octahedral compound in solid state and this magnetic susceptibility value is larger than the spin-only value expected for a high spin  $d^7$  ion ( $S = 3/2$ ,  $3.87 \mu\text{B}$ ). This accounts for the presence of three unpaired electrons in solid state at room temperature. We have also performed EPR analysis at RT and LT (77 K) using single crystals of this cobalt compound but the spectrum remained silent in both phases. Now, in general high-spin octahedral cobalt(II) ion has a  ${}^4\text{T}_{1g}$  ground state. The magnetic moments of cobalt(II) complexes with T ground terms are often found to show considerable temperature dependence, and interpreting them is very difficult because the angular orbital momentum is partially quenched.<sup>26,27</sup> Due to large spin-orbit coupling, these systems exhibit substantial zero field splitting, which causes high magnetic anisotropy<sup>28–30</sup> and causes very strong spin lattice relaxation time for the high spin cobalt(II) complexes.<sup>29</sup> In general, few cobalt complexes which show EPR signal at RT/LT were low spin cobalt complexes like cobalt-phthalocyanine of square planar geometry. Literature survey indicates, high spin pure cobalt(II) compounds in octahedral geometry give rise to valuable information only at



**Figure 3.** UV–Vis spectrum of  $[\text{Co}(\text{phen})_2\text{Cl}_2]$  (**1**) in water. *Inset* Expansion of UV–Vis spectrum of **1** from 450 to 700 nm in water medium [ $10^{-4}$  M, 1 cm optical path length].

liquid helium temperature (4 K) but variable temperature magnetic measurement may lead to more insight about the electronic spin nature of this cobalt(II)-phenanthroline complex.<sup>26–30</sup>

We have made a comparison between the spectral profiles of the reported octahedral cobalt(II) compound and our compound which reveals the spin configuration of our cobalt(II) compound in solution phase. The interpretation of the visible spectra for the octahedral cobalt(II) is still difficult in spite of existence of a large number of cobalt(II) compounds.<sup>31</sup> The origin of visible spectra for cobalt(II) compounds may be due to spin-orbit coupling, vibrational or low symmetry components, and contribution of these parameters bring difficulties in the total spectral analyses of six-coordinated cobalt(II) complexes.<sup>31</sup> Kundu *et al.*,<sup>32</sup> showed that an octahedral cobalt(II) compound having  $\text{CoN}_4\text{O}_2$  chromophore exhibits a distinct absorption band at 521 nm which corresponds to the high spin octahedral cobalt(II) environment. Kapoor *et al.*,<sup>33</sup> produced a series of octahedral cobalt(II) compounds and found broad absorption band at  $\sim 550$  nm. Handel *et al.*,<sup>34</sup> observed absorption band at  $\sim 480$  nm for cobalt(II) compounds containing tridentate N-donor Schiff base ligand and inferred in favour of octahedral high spin cobalt(II) compounds. Herein, in our absorption spectrum (Figure 3) in aqueous medium, we observed three characteristic spectral bands: 240–270, 353, 530–600 nm (very broad). Among the three bands, two strong transitions in the UV region are of ligand centered and assigned to  $\pi - \pi^*$  on  $n - \pi^*$  transitions in the pyridine rings of phenanthroline ligand. A weaker broad absorption band  $\sim 550$  nm was observed in aqueous medium and assignable to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  electronic transition which is a characteristic of high spin octahedral cobalt(II) environment. Electron spray ionization mass spectral study was also performed which confirmed the molecular existence of the cobalt(II) compound in



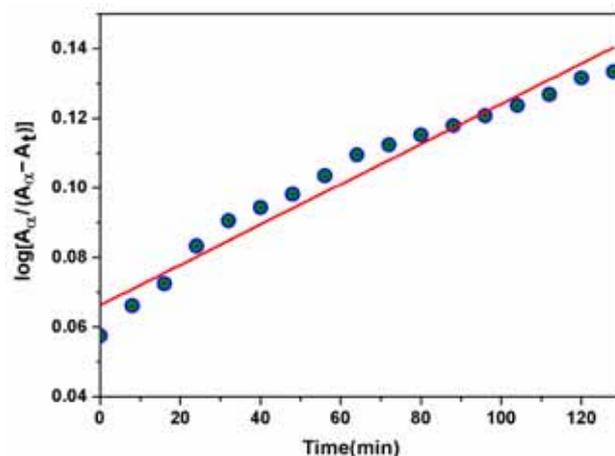
**Figure 4.** Increase of 4-nitrophenolate band at 423 nm after addition of 100 equivalents of PNPP to  $[\text{Co}(\text{phen})_2\text{Cl}_2]$  (**1**) solution in aq. DMF medium. The spectra were recorded after every 9 min.

aqueous medium: ESI-MS ( $\text{H}_2\text{O}$ ):  $m/z$ , 438.68 (Calc. 438.08).

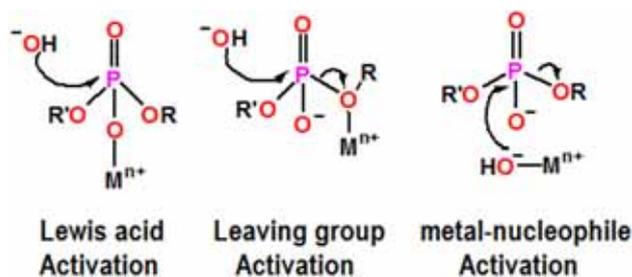
### 3.4 Phosphatase activity of $[\text{Co}(\text{phen})_2\text{Cl}_2]$ (**1**) and its mechanistic implications

We have followed the changes in the spectral features of the Co(II)-phen complex upon the addition of PNPP using spectrophotometrically and the observations are shown in Figure 4, where the spectra were recorded for 2 h at 9 min intervals. In order to examine the hydrolytic cleavage efficiency of phosphoester bonds in aqueous DMF, we have monitored the time evolution of 4-nitrophenolate ( $\lambda_{\text{max}} = 416 \text{ nm}$ ) through a wavelength scan from 200 to 900 nm at  $25^\circ\text{C}$ , containing 100 equivalents of substrate relative to the catalyst, until roughly 2% reaction conversion was reached.

The kinetics study was performed using the initial slope method, following the rate of increase in the absorption of the band at 416 nm corresponding to a rise of 4-nitrophenolate concentration. The initial first order rate constant,  $k_{\text{obs}} (\text{min}^{-1}) = 5.78 \times 10^{-4}$  (Error =  $4.90 \times 10^{-5}$ ) for the cleavage of PNPP was obtained from the plot of  $\log[A_\alpha/(A_\alpha - A_t)]$  versus time (Figure 5) which was linear with  $R^2 = 0.9519$ . The kinetic parameters ( $V_{\text{max}}$ ,  $k_M$ ,  $k_{\text{cat}}$ ) for the catalyzed reactions were determined by applying Michaelis–Menten eq. for enzymatic kinetics and found as follows:  $V_{\text{max}} = 1.055 \times 10^{-4} (\pm 1.98 \times 10^{-5})$ ,  $k_M = 4.27 \times 10^{-3} (\pm 1.21 \times 10^{-4})$  (Figure S2 in Supplementary Information). Turn over number for this hydrolytic catalysis was determined as  $k_{\text{cat}} = 3.78 \times 10^2 \text{ h}^{-1}$ . To confirm the non-catalytic properties of the ligand, control experiments were performed



**Figure 5.** Initial rate determination using plot of  $\log[A_\alpha/(A_\alpha - A_t)]$  versus time.

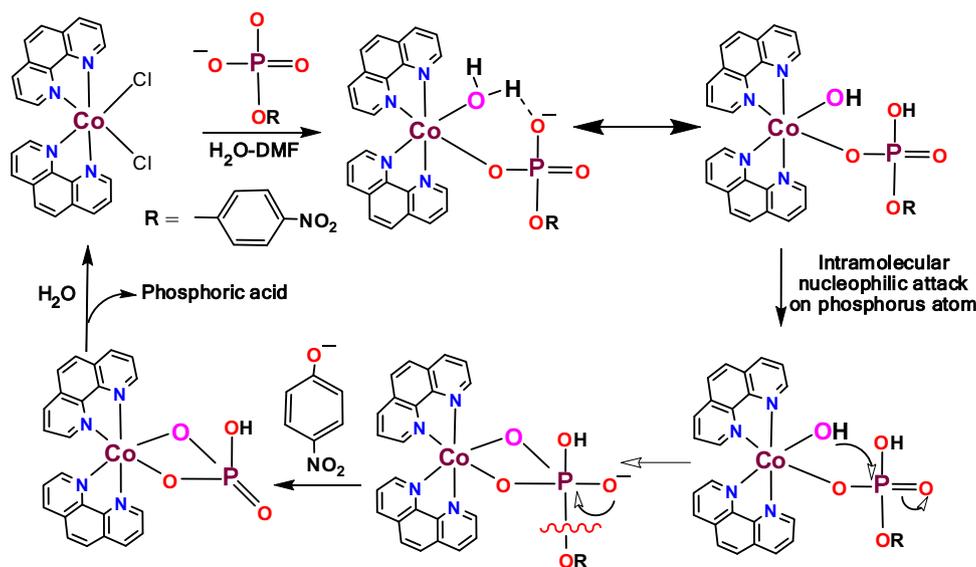


**Scheme 2.** Modes by which phosphates are activated by metal ions.

and found to be non-responsive towards PNPP hydrolysis.

We have taken careful measure to propose the cleavage mechanism of PNPP for our cobalt(II) complex from the reported scientific literature.<sup>35–39</sup> It is seen that metal catalysts can take significant initiative for catalytic cleavage of PNPP through Lewis acid activation, metal-nucleophile attack and leaving group activation (Scheme 2), and exhibit remarkably fast rates of phosphate hydrolysis. Rate of acceleration for the catalytic phenomenon is observed when multiple assisting parameters are working concurrently.<sup>35–38</sup> After rigorous review of the scientific literature, herein, we propose the plausible catalytic cycle having reasonably good agreement with our kinetic result. The generation of nucleophile from coordinated water molecules at the metal centres in the reaction medium remains the fundamental aspect in this catalysis which later follows the attack of metal bound nucleophile on phosphorous atom, as a representative mechanism (Scheme 3).

In aqueous DMF solution, metal coordinated nitrate ion gets dissociated from Co(II)-phen complex. Here, in solution, metal coordinated water molecule plays the most significant role to facilitate hydrolytic cleavage



**Scheme 3.** Plausible mechanistic pathway for PNPP hydrolysis promoted by Co(II)-phen complex.

of PNPP. Addition of PNPP to Co(II)-phen complex occurred in a monodentate fashion which is further established probably through O<sup>−</sup>⋯H interactions between anionic oxide ion with H atom of the coordinated water molecule. At this stage, the coordinated water molecule deprotonates to yield a hydroxide ion as the potent nucleophile leading to an intermediate which is further consolidated in ESI-MS study as a major signal at *m/z* of 534.06 (Figure S3 in Supplementary Information). It is followed by the formation of an organophosphorus intermediate by nucleophilic substitution reaction with the concomitant expulsion of *p*-nitrophenolate ion. It then gradually breaks down into the original complex and phosphoric acid.

Phosphoesterase mimics by cobalt(II) complexes are not extensively studied and a few comparative studies of phosphoester cleavage is available in recent literature.<sup>40–43</sup> Previous studies have suggested that the coordinated alcohol is deprotonated at higher pH or coordinated water molecule<sup>44</sup> below the same pH. Both the coordinated alcohol and water molecule act as effective nucleophiles.<sup>45,46</sup> However, in our complex, solvent aqua molecules displaced the labile chloride ions and behaved as effective nucleophile towards phosphoester cleavage activity.<sup>44</sup>

#### 4. Conclusions

Herein, we report a synthesis and structural characterization of a [Co(phen)<sub>2</sub>Cl<sub>2</sub>] compound under N<sub>2</sub> atmosphere. Room temperature magnetic susceptibility of this cobalt(II)-phenanthroline complex in powder

state indicates the existence of three-electron high spin state. A comparison of UV–Vis spectrum between our cobalt(II) complex with other cobalt(II) complexes further confirm the spin state. The cobalt(II) complex has been evaluated as a functional model for phosphatase enzyme by using 4-nitrophenylphosphate (PNPP) as a standard substrate in aqueous DMF medium. This cobalt(II) complex exhibits good hydrolytic phosphoester cleavage efficiency and *k*<sub>cat</sub> value is 3.78 × 10<sup>2</sup> h<sup>−1</sup>.

#### Supplementary Information (SI)

Supplementary crystallographic data are available free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>) upon request, quoting deposition number CCDC 1528654. FTIR, UV–Vis spectra, ESI-MS, rate vs concentration of PNPP, and table of crystallographic parameters are given in supplementary information, available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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