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FULL PAPER

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Two mononuclear cobalt(III) complexes exhibiting phenoxazinone synthase activity

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Two mononuclear cobalt(III) complexes, namely [LCo(tmtp)(H_2O)]ClO_4·MeOH (**1**) (tmtp = tri(*m*-tolyl)phosphine) and [LCo(PPh_3)(H_2O)]PF_6 (**2**), have been prepared from a polydentate ligand, *N*,*N*′-bis(3-methoxysalicylidehydene)cyclohexane-1,2-diamine (**H_2L**). Standard analytical techniques such as elemental analysis and UV–visible and Fourier transform infrared spectroscopies were used to characterize both complexes. The solid-state molecular structures of both complexes were confirmed from single-crystal X-ray diffraction analysis. Structural analyses show that the Co(III) ion occupies the centre of a distorted octahedron in a complex cation: [LCo(tmtp)(H_2O)]$^+$ and [LCo(PPh_3)(H_2O)]$^+$ for **1** and **2**, respectively. Phenoxazinone synthase activities of both complexes were screened. Kinetic studies and other experimental observations reveal that the reaction follows rate saturation kinetics and proceeds through the formation of a catalyst (complex)–substrate adduct. The turnover number (K_{cat}) of complex **2** is 54.07 h^{-1}, exhibiting better catalytic activity compared to **1** (K_{cat} = 45.11 h^{-1}).

KEYWORDS
cobalt(III) complex, phenoxazinone synthase activity, Schiff base, single-crystal X-ray diffraction, turnover number

1 | INTRODUCTION

Schiff bases cover an enormous area in coordination chemistry predominantly due to their smooth synthesis, controllability of steric and electronic environment and diversity in applications.[1] Schiff bases can easily accommodate single or multiple metal ions of various oxidation states.[2] Judicial selection of Schiff bases and metal ions often results in homo- or heteronuclear metal complexes including those of transition metals and main group elements.[3] Depending on the nature of the ligands and metal ions, these complexes exhibit structural diversities and open up applications in several areas such as biology,[4] catalysis,[5] materials science[6] and magnetism.[7] Interestingly, salen-type ligands, which are prepared from various diamines and salicylaldehyde derivatives, are most widely explored among all Schiff bases in coordination chemistry.[8] Modification of salicylaldimine ligands, for example by anchoring a methoxy group (—OMe) on the salicylaldimine moiety, increases their denticity making the ligands more prone to form polynuclear complexes.[9] Numerous examples of metal complexes of Schiff base ligands have been reported in the literature. However, metal complexes containing cobalt(II/III) ions have recently started to receive attention.[10] Cobalt(II/III) complexes of Schiff base ligands find important applications in magnetism,[11] biochemistry[12] and catalysis.[13] These complexes have been used in mimicking important biological co-factors such as phenoxazinone synthase,[14] photosynthesis,[15] methionine aminopeptidase,[16] cobalamin, etc. Among these, phenoxazinone synthase facilitates the conversion of *o*-aminophenol

(OAPH) to 2-aminophenoxazine-3-one (APX) during the synthesis of actinomycin D which is renowned for the treatment of gestational choriocarcinoma, Wilms tumour, rhabdomyosarcoma, etc.[17] Although the active site of phenoxazinone synthase contains five Cu(II) ions responsible for conversion of OAPH to APX,[18] several catalysts (complexes) containing Co(II/III) centres have been developed as model systems to understand the role of phenoxazinone synthase in such a conversion.[19] Scheme 1 shows the conversion of OAPH to APX. Several mechanistic pathways are available for such a conversion. However, the most widely accepted one involves a quinone imine intermediate (I), which combines with a second molecule of OAPH resulting in an intermediate (II), which is then converted to *p*-quinoneimine (III) upon two-electron oxidation processes. Finally, a phenoxazinone chromophore is obtained by another conjugate addition and subsequent two-electron oxidation of it.[20]

While working with a Schiff base ligand, *N*,*N*′-bis(3-methoxysalicylidehydene)cyclohexane-1,2-diamine (**H_2L**), we have recently reported several homo- or heteronuclear Ni(II)–Na(I), Co(III)–Na(I) and Co(III) complexes. We have also investigated the biological activity of the Ni(II)–Na(I) complex.[21] In addition, we were able to show phenoxazinone synthase activities of two Co(III) complexes of **H_2L**.[22] In the work reported in the present contribution, we used the ligand **H_2L** to synthesize two new mononuclear Co(III) complexes, [LCo(tmtp)(H_2O)]ClO_4·MeOH (**1**) (tmtp = tri(*m*-tolyl)phosphine) and [LCo(PPh_3)(H_2O)]PF_6 (**2**) (PPh_3 = triphenylphosphine). The solid-state molecular structures of both complexes were investigated using single-crystal X-ray diffraction analyses. The complexes were further characterized using elemental analyses and UV–visible and Fourier transform infrared (FT-IR) spectroscopies. Phenoxazinone synthase activities of complexes **1** and **2** were investigated. Various important kinetic parameters such as V_{max}, K_M and K_{cat} were evaluated.

2 | EXPERIMENTAL

2.1 | General and Analytical Techniques

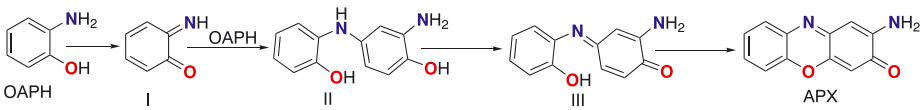
All chemical reactions were executed under aerobic conditions. All reagents employed in the present work were of analytical grade and obtained from Sigma Aldrich, India, or Alfa Aesar, India. Distilled solvents were used in all experimental work. The ligand **H_2L** was synthesized following a reported process.[23] Elemental (C, H and N) analyses were performed with a FLASH EA 1112 series (Thermo Finnigan, Italy). FT-IR spectra were recorded with a Cary 600 series FT-IR spectrometer in the range 400–4000 cm^{-1}. A Shimadzu UV-1800 spectrometer was used to record the absorption spectra of all complexes in methanol. Electrospray ionization mass analyses were carried out with a Waters UPLC-TQD mass spectrometer.

2.2 | Synthesis of 1

A solution of **H_2L** (0.1911 g, 0.5 mmol) in 10 ml of methanol was added to a solution of $Co(OAc)_2·4H_2O$ (0.1245 g, 0.5 mmol) in methanol (10 ml). The mixture immediately turned brown and was stirred for 15 min. Tri(*m*-tolyl)phosphine (0.1522 g, 0.5 mmol) was added to it and stirred for 1 h with bubbling air. Solid $NaClO_4$ (0.0702 g, 0.5 mmol) was added to the mixture and stirred for an additional 0.5 h. The resulting mixture was filtered and kept for slow evaporation at room temperature in open atmosphere. Dark green single crystals suitable for single-crystal X-ray diffraction analysis were achieved after 13 days. Yield 0.3532 g (79%). Anal. Calcd for $C_{44}H_{51}ClCoN_2O_{10}P$ (molecular weight: 893.21) (%): C, 59.16; H, 5.75; N, 3.14. Found (%): C, 58.21; H, 3.96; N, 3.05. FT-IR (ATR, cm^{-1}): 3354 (m), 2932 (m), 2855 (w), 1623 (s), 1550 (w), 1445 (s), 1312 (s), 1221 (s), 1078 (s), 976 (m), 860 (w), 777 (w), 737 (m), 690 (m), 618 (w), 553 (m), 452 (m).

2.3 | Synthesis of 2

A solution of **H_2L** (0.1911 g, 0.5 mmol) in 10 ml of methanol was added to a solution of $Co(OAc)_2·4H_2O$ (0.1245 g, 0.5 mmol) in methanol (10 ml). The mixture immediately turned brown and was stirred for 15 min. Triphenylphosphine (0.1311 g, 0.5 mmol) was added to it and stirred for 1 h with bubbling air. Solid KPF_6 (0.092 g, 0.5 mmol) was added to the mixture and stirred for an additional 0.5 h. The resulting mixture was filtered and kept for slow evaporation at room temperature in open atmosphere. Dark green single crystals suitable for single-crystal X-ray diffraction analysis were obtained after 18 days. Yield 0.3312 g (74 %). Anal. Calcd for $C_{40}H_{41}CoF_6N_2O_5P_2$ (molecular weight: 864.62) (%): C, 55.56; H, 4.78; N, 3.24. Found (%): C, 54.50; H, 3.41; N, 3.53. FT-IR (ATR, cm^{-1}): 3370 (m), 2934 (w), 2867 (w),

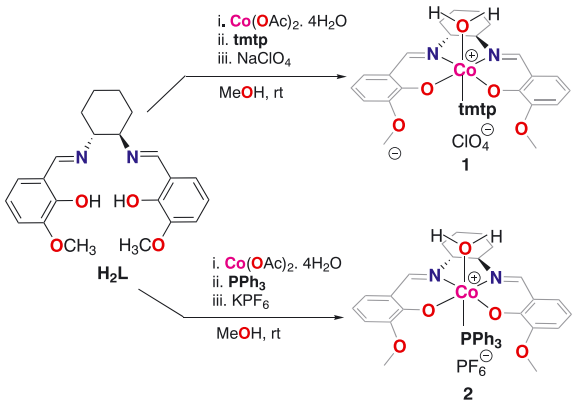


SCHEME 1 Conversion of *o*-aminophenol (OAPH) to 2-aminophenoxazine-3-one (APX)

1624 (s), 1604 (s), 1551 (m), 1470 (m), 1438 (s), 1317 (s), 1248 (s), 1220 (s), 1090 (s), 1030 (m), 977 (m), 836 (s), 734 (m), 693 (m), 556 (m), 518 (m).

2.4 | Phenoxazinone Synthase Activity Study

The phenoxazinone synthase activities of complexes **1** and **2** were investigated by reacting them (1×10^{-5} M) with OAPH (1×10^{-3} M) in methanol (25 °C). The progress of the reaction was monitored by measuring the increase in absorbance at 433 nm as a function of time. To determine important kinetic parameters and to evaluate dependence of the reaction rate on substrate concentration, a solution of catalyst (1×10^{-5} M) in methanol was treated with a set of solutions of the substrate in methanol (1×10^{-3}–10×10^{-3} M). Initially, stock solutions of OAPH as well as complexes of desired concentrations were prepared by dissolving calculated amounts of them in 10 ml of methanol. Then, 2 ml of each OAPH solution was added to 0.5 ml of catalyst solution to achieve concentrations of 1×10^{-3}–10×10^{-3} M for OAPH and 1×10^{-5} M for catalysts in a solution of total volume of 2.5 ml. Initial rate was calculated from the absorbance value recorded at 150 s after addition of the solutions.



SCHEME 2 Synthesis of complexes **1-2**

2.5 | X-ray Crystallography

Single crystals of **1** and **2** suitable for X-ray diffraction were mounted on an Oxford Diffraction XCalibur Eos instrument equipped with Cu Kα radiation (λ = 1.54184 Å) and Mo Kα radiation (λ = 0.71073 Å) at T = 100(2) K, respectively. CrysAlisPro software was used for data collection and data reduction. The structure was solved by direct methods (SIR92)[24] followed by refinement on F^2 by full-matrix least-squares methods using SHELXL-2013.[25] Non-hydrogen atoms such as C, P, N, O, Cl, F and Co were refined anisotropically. Hydrogen atoms were included using appropriate AFIX command. The function minimized was $\left[\Sigma w\left(F_o^2-F_c^2\right)^2\right]$ $(w = 1/\left[\sigma^2\left(F_o^2\right) + (aP)^2 + bP\right])$, where $P = \left(\mathrm{Max}\left(F_o^2, 0\right) + 2F_c^2\right)/3$ with $\sigma^2\left(F_o^2\right)$ from counting statistics. The functions R_1 and wR_2 were $(\sigma||F_o| - |F_c||)/\sigma|F_o|$ and $[\sigma w\left(F_o^2-F_c^2\right)^2/\sigma(wF_o^4]^{1/2}$, respectively. Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1579029-1579030. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

3 | RESULTS AND DISCUSSION

3.1 | Synthesis

The procedure for the synthesis of the Schiff base ligand **H_2L** was previously established.[23] **H_2L** was prepared

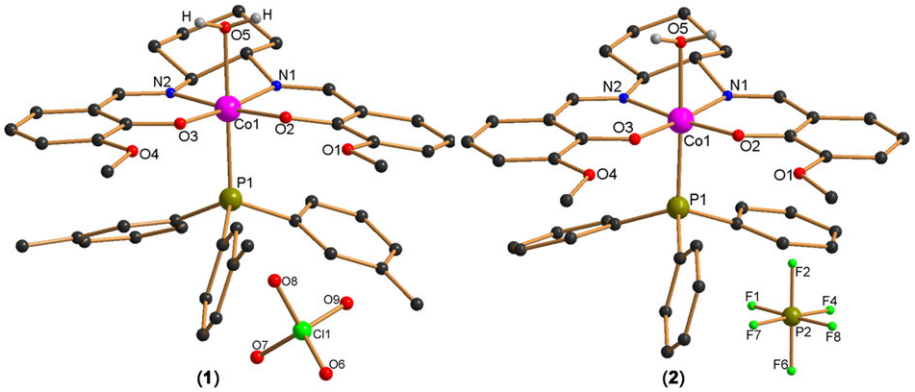


FIGURE 1 Molecular structures of complexes **1** and **2**. Hydrogen atoms of the ligands, as well as a methanol solvent molecule are omitted for clarity

by refluxing *o*-vanillin with 1,2-diaminocyclohexane in ethanol. Two mononuclear Co(III) complexes **1** and **2** were prepared by reacting **H_2L** with cobalt(II) acetate tetrahydrate in the presence of tmtp and PPh_3, respectively (Scheme 2). Additionally, anions perchlorate (ClO_4^-) or hexafluorophosphate (PF_6^-) were employed for neutralizing the charge of cationic complexes in these compounds. Detailed synthetic processes for complexes **1** and **2** are described in Section 1.

Both complexes were dark green in colour, stable in air and soluble in standard organic solvents. Successful syntheses of **1** and **2** were established using various analytical techniques, for instance, FT-IR spectroscopy, elemental analysis and UV–visible spectroscopy. In addition, solid-state molecular structures of **1** and **2** were confirmed using single-crystal X-ray diffraction analyses.

TABLE 1 Single-crystal data and structure refinement parameters for complexes **1** and **2**

	1	2
Formula	$C_{44}H_{51}ClCoN_2O_{10}P$	$C_{40}H_{41}CoF_6N_2O_5P_2$
Formula mass	893.21	864.62
T (K)	100(2)	100(2)
λ (Å)	1.54184	0.71073
Crystal dimensions (mm)	0.22 × 0.14 × 0.05	0.22 × 0.15 × 0.11
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	12.4463(3)	13.8631(5)
b (Å)	20.4390(5)	17.1662(7)
c (Å)	18.8469(5)	16.6104
β (°)	119.063(2)	110.385(10)
V (Å^3)	4190.8(2)	3705.3(2)
Z	4	4
D_c (g cm^{-3})	1.416	1.550
μ (mm^{-1})	4.667	0.629
F(000)	1872.0	1784.0
2θ range (°)	6.892–150.727	4.746–55.106
Measured reflections	40 388	36 332
Independent reflections/R_{int}	8486/0.0708	8531/0.0267
Parameters	547	531
R_1 ($I > 2\sigma(I)$)	0.0698	0.0464
wR_2 (all data)	0.2054	0.1116
Goodness-of-fit on F^2	1.072	1.032
$\Delta\rho_{max,min}$, e Å^{-3}	1.03, −0.62	0.83, −0.84

3.2 | FT-IR Spectroscopy

The FT-IR spectra of complexes **1** and **2** show a characteristic band of azomethine (—C=N) stretching at 1623 and 1624 cm^{-1}, respectively (Figures S1 and S2).[26] These bands are shifted to lower energy compared to the free ligand (1631 cm^{-1}; Figure S3) confirming the coordination of the azomethine nitrogen to the cobalt(III) ion in these complexes. A broad band due to —OH (of a coordinated water molecule) stretching appears at approximately 3350 cm^{-1} for both complexes. An intense band observed at around 1078 cm^{-1} is assigned to the stretching vibration of a non-coordinated ClO_4^- anion in **1**.[19c, 26c] The spectrum of complex **2** exhibits a moderate band at 836 cm^{-1} caused by stretching vibration of the PF_6^- anion.[27] In addition, aliphatic C—H stretching resonances are observed in the range 2933–2937 cm^{-1} for both complexes.

3.3 | Description of Structures

Single-crystal X-ray diffraction was employed to determine the solid-state structures of complexes **1** and **2**. Both complexes crystallize in the monoclinic space group $P2_1/c$ with four formula units per unit cell. The solid-state

TABLE 2 Selected bond lengths (Å) and bond angles (°) of complexes **1** and **2**

	1	2
Co1–N1	1.899(3)	1.898(2)
Co1–N2	1.899(3)	1.8933(18)
Co1–O2	1.900(3)	1.8825(15)
Co1–O3	1.899(3)	1.8880(15)
Co1–O5	2.051(2)	2.0609(16)
Co1–P1	2.253(11)	2.2456(6)
N1–Co1–N2	85.86(14)	85.67(8)
N1–Co1–O2	93.11(13)	93.48(8)
N2–Co1–O3	94.63(13)	94.55(7)
O2–Co1–O3	85.84(11)	85.87(7)
O2–Co1–O5	87.41(11)	88.15(7)
O3–Co1–O5	87.77(11)	87.78(7)
N1–Co1–O5	86.01(12)	87.63(9)
N2–Co1–O5	87.39(12)	86.61(7)
O2–Co1–P1	90.68(8)	90.72(5)
O3–Co1–P1	89.92(9)	88.00(5)
N1–Co1–P1	96.26(10)	96.59(7)
N2–Co1–P1	94.55(10)	94.55(6)
O5–Co1–P1	177.10(8)	175.70(5)

molecular structures of **1** and **2** are shown in Figure 1. Detailed data for the X-ray diffraction analysis are provided in Table 1. Each complex contains a Co(III) ion occupying the N_2O_2 cavity of a deprotonated ligand (L^{2-}). One molecule of water and tmtp (**1**) or PPh_3 (**2**) are bonded to the Co(III) centre axially, thus resulting a distorted octahedral geometry around it. The complex cations $[LCo(tmtp)(H_2O)]^+$ and $[LCo(PPh_3)(H_2O)]^+$ are associated with a perchlorate (ClO_4^-) and hexafluorophosphate (PF_6^-) anions, for **1** and **2**, respectively. Moreover, a molecule of methanol can be found in **1** as solvent of crystallization. The Co—N and Co—O bond lengths in the N_2O_2 plane of the ligand are 1.899(3) and 1.889(3)–1.900(3) Å in **1** and 1.8933(18)–1.898(2) and 1.8825(15)–1.8880(15) Å in **2**, respectively.[28] The Co—O_{axial} (O5) bond lengths are 2.051(2) and 2.0609(16) Å, in complexes **1** and **2**, respectively. As anticipated, the Co—O_{axial} bond length is longer than the Co—$O_{equitorial}$ bond length. The Co—P bond lengths of 2.2456(6) and 2.2538(11) Å in **1** and **2** are close to reported values.[28] Selected bond lengths and angles are given in Table 2.

3.4 | UV–Visible Absorption Spectroscopy

UV–visible spectra of complexes **1** and **2** were recorded in methanol in the range 200–1100 nm at ambient temperature. The absorption spectra (200–600 nm) of complexes **1** and **2** are shown in Figure 2. Absorption bands because of intra-ligand π–π^* electronic transitions are observed in the high-energy region of 250–307 nm for both complexes. A high-energy band at around 410 nm is attributed to ligand-to-metal charge transfer transition.[29] In addition to that, the spectra of both complexes show anticipated d–d transition bands. For an octahedral Co(III) complex, the two expected d–d transition bands are those of $^1A_{1g} \rightarrow T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively.[30] A band at approximately 760 nm (Figure S4) is assigned to low-energy $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. However, high-energy $^1A_{1g} \rightarrow {}^1T_{2g}$ transition is not observed in the UV–visible region. Possibly, the high-energy charge transfer transition has masked the expected d–d transition in that region.

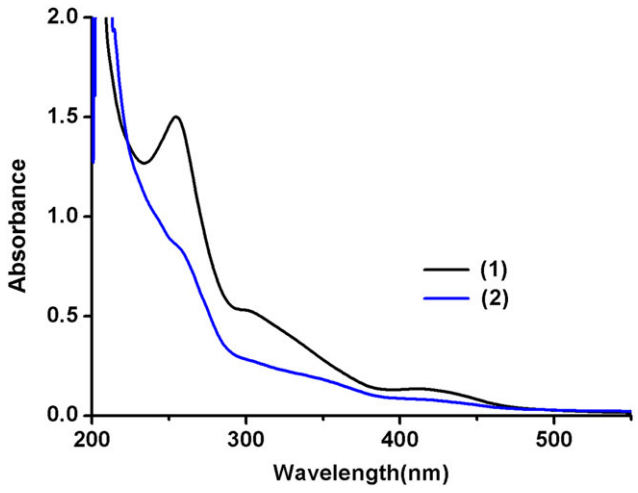


FIGURE 2 UV–visible spectra of complexes **1** and **2**

3.5 | Phenoxazinone Synthase Activity and Kinetic Studies

Conversion of OAPH to APX is generally monitored by UV–visible spectroscopy. The change in absorbance due to the formation of APX in the reaction mixture is recorded at 433 nm. Therefore, a gradual increase in absorbance with time implies the formation of APX in solution. In the present study, the growth of the

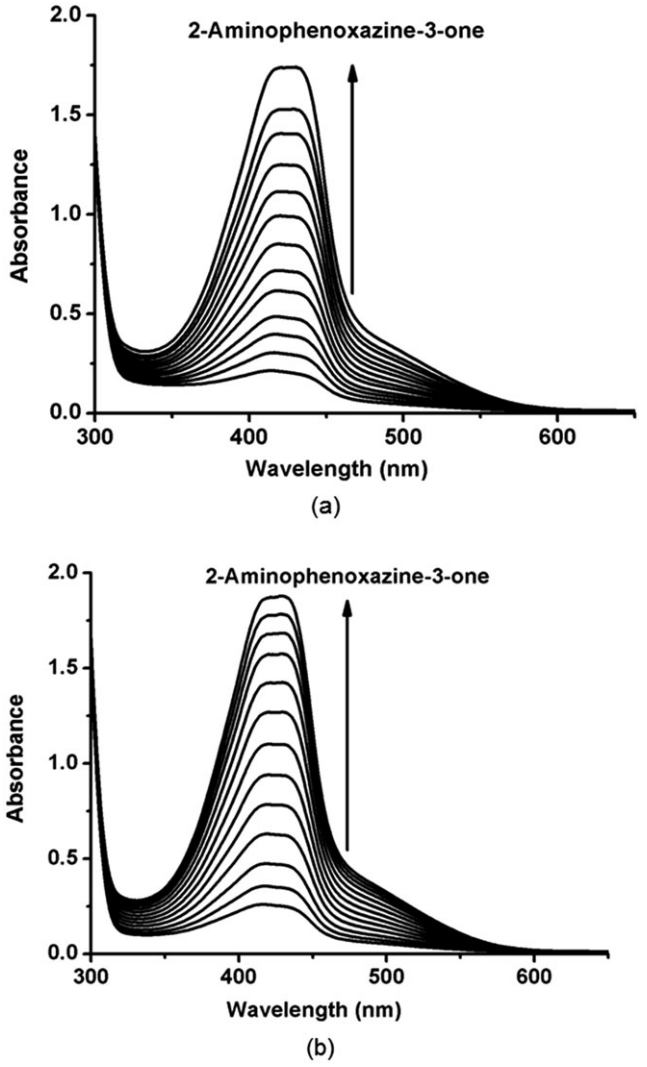


FIGURE 3 Increase in absorption of 2-aminophenoxazine-3-one at 433 nm after addition of 0.01 M OAPH to a solution containing (a) complex **1** and (b) complex **2** in methanol up to 2.5 h under aerobic condition at 25 °C

phenoxazinone chromophore of a solution of 1×10^{-3} M OAPH and 1×10^{-5} M of respective complexes (**1** and **2**) using methanol as solvent was recorded under aerobic conditions at temperature 25 °C for 2 h with an interval of 10 min (Figure 3). Base was not added to avoid autoxidation of OAPH. A blank test was performed in the absence of catalyst under identical experimental conditions. No significant amount of APX is observed (Figure S5) supporting the role of catalyst in such reaction.

Further, kinetic studies were performed using OAPH as substrate and complexes **1** and **2** as catalysts. Under aerobic conditions, a solution (1×10^{-5} M) of each catalyst was mixed with 1×10^{-3}–10×10^{-3} M solution of OAPH in methanol. It was observed that the reactions follow pseudo-first-order kinetics. Plots of the initial rates of these reactions against the concentration of OAPH for both complexes are depicted in Figure 4, which shows rate saturation kinetics for both complexes. Such a finding is often observed in enzyme catalysis, where a moderately stable enzyme (catalyst)–substrate adduct is formed, which follows a Michaelis–Menten equation. The linearization of the Michaelis–Menten equation results in a Lineweaver–Burk plot (Figure 4, insets) from which various important parameters such as K_M (Michaelis constant) and V_{max} (maximum reaction velocity) are determined. These values are listed in Table 3. The turnover numbers of both complexes are in the range of those of previously reported Co(III) complexes.[19c, 22, 31] Complex **2**, with a K_{cat} value of 54.07 h^{-1}, exhibits better catalytic activity compared to **1** ($K_{cat} = 45.11$ h^{-1}).

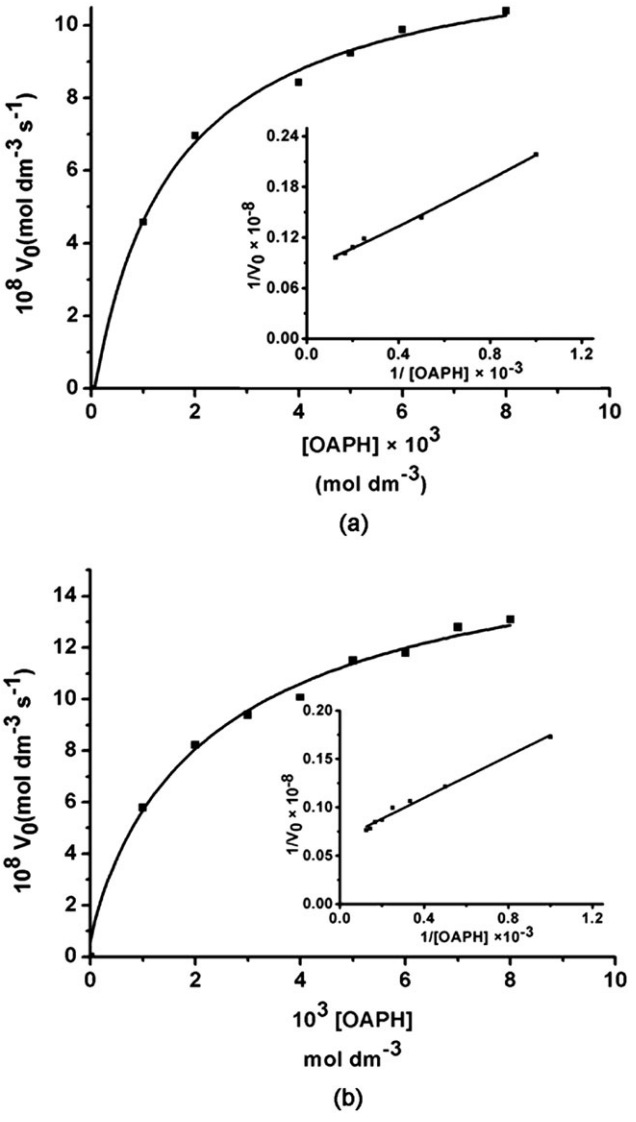


FIGURE 4 Plot of initial rate versus substrate concentration in the conversion of OAPH to APX in methanol for (a) complex **1** and (b) complex **2**. Respective double reciprocal or Lineweaver–Burk plots are shown in the insets

3.6 | Mass Spectrometry

The electrospray ionization (ESI) mass spectra of a mixture of OAPH and respective complexes (100:1) were recorded using methanol as solvent within 5 min of addition of methanol to the mixture. The spectra are presented in Figures S6–S9 in the supporting information. The formation of APX chromophore was ascertained by the appearance of a peak at $m/z \sim 213.57$ for both complexes. A peak at $m/z = 439.54$ indicates the formation of $[Co(L)]^+$ for both complexes. Complex cationic fragments $[LCo(tmtp)]^+$ and $[LCo(PPh_3)]^+$ were observed at $m/z =$ 743.44 and 701.50 for complexes **1** and **2**, respectively.

TABLE 3 Kinetic parameters for complexes **1** and **2**

Complex	V_{max}	K_M	K_{cat} (h^{-1})
1	12.53×10^{-8}	1.719×10^{3}	45.11
2	15.02×10^{-8}	1.624×10^{3}	54.07

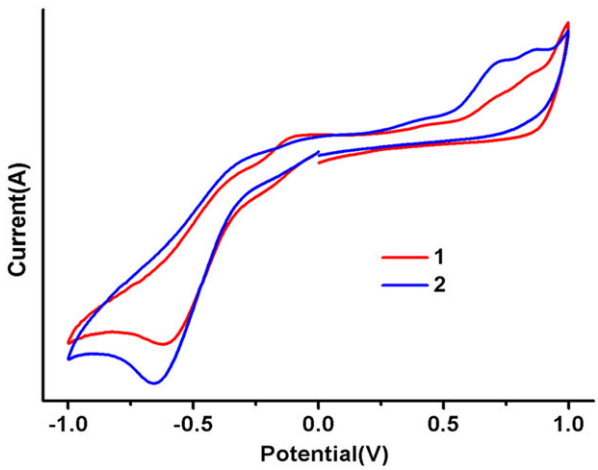
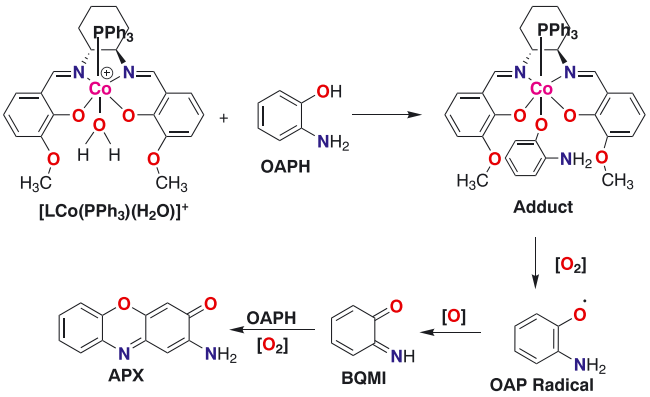


FIGURE 5 Cyclic voltammograms of **1** and **2** in methanol



SCHEME 3 Probable mechanistic pathway for the conversion of 2-aminophenol to phenoxazinone chromophore

Moreover, the formation of catalyst–substrate adducts $[LCo(tmtp)(OAP)]^+$ and $[LCo(PPh_3)(OAP)]^+$ are confirmed by the peaks at m/z = 853.40 and 808.41 for **1** and **2**, respectively.

3.7 | Electrochemical Studies

Being susceptible to reduction and oxidation, the electrochemical properties of Co(III/II) systems are of prime interests. The electrochemical data for both complexes were collected by maintaining a concentration of 1 mmol for the complexes in methanol along with 0.1 M solution of tetrabutylammonium bromide as electrolyte with a scan rate of 100 mV s^{-1} in aerobic environment. A platinum electrode functioned as the working electrode while Ag/AgCl served as the reference electrode. Figure 5 shows the cyclic voltammograms of complexes **1** and **2**. Peaks were obtained at −0.62 and −0.65 V which correspond to reduction of Co(III) to Co(II) for complexes **1** and **2**, respectively. These results indicate that both complexes may not be suitable for catalysing any oxidation reactions under aerobic condition in methanol. However, their electrochemical behaviour may be influenced by the formation of substrate–catalyst adduct, thus favouring oxidation of OAPH in methanol. Additionally, the negative potential favours regeneration of Co(III) catalyst via oxidation of Co(II) under the experimental conditions.

3.8 | Probable Mechanism

Now, it is established that complexes **1** and **2** dissociate in methanol to generate $[LCo(tmtp)]^+$ and $[LCo(PPh_3)]^+$, respectively. These are the active forms of **1** and **2** responsible for catalytic conversion of OAPH to APX. It is also evident from the kinetic studies and mass spectral analysis that conversion of OAPH to APX proceeds through the formation of a catalyst–substrate adduct, i.e. $[LCo(tmtp)(OAP)]^+$ and $[LCo(PPh_3)(OAP)]^+$ for complexes **1** and **2**, respectively. Based on these experimental observations, a mechanism for the conversion of OAPH to APX chromophore catalysed by complex **2** is proposed, as shown in Scheme 3. Initially, complex **2** generates a $[LCo(PPh_3)]^+$ ion in solution which combines with OAPH to form a catalyst–substrate adduct, $[LCo(PPh_3)(OAP)]$, which results in the formation of an OAP radical by reacting with molecular oxygen. The OAP radical converts *o*-benzoquinone monoamine (BQMI), which finally reacts with OAPH and molecular oxygen to yield APX through many oxidative dehydrogenation processes. In order to evaluate the role of molecular oxygen in the conversion of OAPH to APX, the growth of APX at 433 nm was monitored in methanol in an argon atmosphere in the same time span using both complexes. The growth of APX is significantly reduced under such conditions. Therefore, it clearly demonstrates that dioxygen plays an important role in such catalytic conversion.

4 | CONCLUSIONS

We have successfully synthesized two mononuclear Co(III) complexes of a polydentate Schiff base ligand (H_2L). The Co(III) ion is positioned in the N_2O_2 cavity of the ligand. Both complexes ionize in a solution of methanol and exhibit excellent phenoxazinone synthase activity. Kinetic studies and ESI-MS analysis indicate that the conversion of 2-aminophenol to the phenoxazinone chromophore passes through the formation of a catalyst–substrate adduct. Complex **2** shows better (K_{cat} = 54.07 h^{-1}) catalytic activity than **1** (K_{cat} = 45.11 h^{-1}).

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REFERENCES

[1] a) M. Rezaeivala, H. Keypour, *Coord. Chem. Rev.* **2014**, *280*, 203; b) R. Ziessel, *Coord. Chem. Rev.* **2001**, *216*, 195.

[2] a) R. Vinayak, A. Harinath, C. J. Gómez-García, T. K. Panda, S. Benmansour, H. P. Nayek, *Chem. Select* **2016**, *1*, 6532; b) S. Saha, S. Pal, C. J. Gómez-García, J. M. Clemente-Juan, K. Harms, H. P. Nayek, *Polyhedron* **2014**, *74*, 1.

[3] a) D. A. Atwood, *Coord. Chem. Rev.* **1997**, *165*, 267; b) M. Nath, P. K. Saini, *Dalton Trans.* **2011**, *40*, 7077; c) S. Saha, A. Sarkar, S. Das, T. K. Panda, K. Harms, H. P. Nayek, *Chemistry Select* **2017**, *2*, 7865; d) S. Saha, A. Harinath, T. K. Panda, H. P. Nayek, *J. Org. Chem.* **2016**, *818*, 37.

[4] S. Saha, S. Jana, S. Gupta, A. Ghosh, H. P. Nayek, *Polyhedron* **2016**, *107*, 183.

[5] a) K. C. Gupta, A. K. Sutar, *Coord. Chem. Rev.* **2008**, *252*, 1420. b) K. C. Gupta, A. Kumar Sutar, C.-C. Lin, *Coord. Chem. Rev.* **2009**, *253*, 1926.

[6] J. Zhang, L. Xu, W.-Y. Wong, *Coord. Chem. Rev.* **2018**, *355*, 180.

[7] a) R. Herchel, I. Nemec, M. Machata, Z. Travnicek, *Dalton Trans.* **2016**, *45*, 18622; b) T. Lacelle, G. Brunet, A. Pialat, R. J. Holmberg, Y. Lan, B. Gabidullin, I. Korobkov, W. Wernsdorfer, M. Murugesu, *Dalton Trans.* **2017**, *46*, 2471.

[8] P. G. Cozzi, *Chem. Soc. Rev.* **2004**, *33*, 410.

[9] M. Andruh, *Dalton Trans.* **2015**, *44*, 16633.

[10] a) L. Pogány, J. Moncol, M. Gál, I. Šalitroš, R. Boča, *Inorg. Chim. Acta* **2017**, *462*, 23; b) F. M. Ashmawy, R. M. Issa, S. A. Amer, C. A. McAuliffe, R. V. Parish, *J. Chem. Soc. Dalton Trans.* **1986**, 421.

[11] Q. Gao, Y. Qin, Y. Chen, W. Liu, H. Li, B. Wu, Y. Li, W. Li, *RSC Adv.* **2015**, *5*, 43195.

[12] X. Li, Z. Liu, Y. Xu, D. Wang, *J. Inorg. Biochem.* **2017**, *171*, 37.

[13] a) M. Caovilla, D. Thiele, R. F. de Souza, J. R. Gregório, K. Bernardo-Gusmão, *Cat. Com.* **2017**, *101*, 85; b) R. J. DiRisio, J. E. Armstrong, M. A. Frank, W. R. Lake, W. R. McNamara, *Dalton Trans.* **2017**, *46*, 10418.

[14] A. Hazari, A. Das, P. Mahapatra, A. Ghosh, *Polyhedron* **2017**, *134*, 99.

[15] T. M. McCormick, B. D. Calitree, A. Orchard, N. D. Kraut, F. V. Bright, M. R. Detty, R. Eisenberg, *J. Am. Chem. Soc.* **2010**, *132*, 15480.

[16] S. L. Roderick, B. W. Matthews, *Biochemistry* **1993**, *32*, 3907.

[17] M. Le Roes-Hill, C. Goodwin, S. Burton, *Trends Biotechnol.* **2009**, *27*, 248.

[18] A. W. Smith, A. Camara-Artigas, M. Wang, J. P. Allen, W. A. Francisco, *Biochemistry* **2006**, *45*, 4378.

[19] a) M. Das, B. N. Ghosh, A. Bauza, K. Rissanen, A. Frontera, S. Chattopadhyay, *RSC Adv.* **2015**, *5*, 73028; b) A. Panja, *Dalton Trans.* **2014**, *43*, 7760; c) K. Ghosh, K. Harms, S. Chattopadhyay, *Polyhedron* **2017**, *123*, 162; d) K. Ghosh, S. Roy, A. Ghosh, A. Banerjee, A. Bauzá, A. Frontera, S. Chattopadhyay, *Polyhedron* **2016**, *112*, 6; e) A. Panja, *Polyhedron* **2014**, *80*, 81.

[20] S. K. Dey, A. Mukherjee, *Coord. Chem. Rev.* **2016**, *310*, 80.

[21] M. Mahato, D. Dey, S. Pal, S. Saha, A. Ghosh, K. Harms, H. P. Nayek, *RSC Adv.* **2014**, *4*, 64725.

[22] M. Mahato, D. Mondal, H. P. Nayek, *Chemistry Select* **2016**, *1*, 6777.

[23] W. Feng, Y. Zhang, X. Lu, Y. Hui, G. Shi, D. Zou, J. Song, D. Fan, W.-K. Wong, R. A. Jones, *Crst. Eng. Comm.* **2012**, *14*, 3456.

[24] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.* **1994**, *27*, 435.

[25] a) G. M. Sheldrick, *Acta Crystallogr. A* **2008**, *64*, 112; b) G. M. Sheldrick, *Acta Crystallogr. C* **2015**, *71*, 3.

[26] a) S. Saha, R. K. Kottalanka, P. Bhowmik, S. Jana, K. Harms, T. K. Panda, S. Chattopadhyay, H. P. Nayek, *J. Mol. Struct.* **2014**, *1061*, 26; b) A. Upadhyay, S. Vaidya, V. S. Venkatasai, P. Jayapal, A. K. Srivastava, M. Shanmugam, M. Shanmugam, *Polyhedron* **2013**, *66*, 87; c) A. A. Dehghani-Firouzabadi, M. Sobhani, B. Notash, *Polyhedron* **2016**, *119*, 49.

[27] M. Salehi, M. Amirnasr, S. Meghdadi, K. Mereiter, H. R. Bijanzadeh, A. Khaleghian, *Polyhedron* **2014**, *81*, 90.

[28] A. H. Kianfar, W. A. Kamil Mahmood, M. Dinari, H. Farrokhpour, M. Enteshari, M. H. Azarian, *Spectrochim. Acta A* **2015**, *136*, 1582.

[29] a) A. Saha, P. Majumdar, S. Goswami, *J. Chem. Soc. Dalton Trans.* **2000**, 1703; b) S. Thakurta, R. J. Butcher, G. Pilet, S. Mitra, *J. Mol. Struct.* **2009**, *929*, 112.

[30] S. Chattopadhyay, M. G. B. Drew, A. Ghosh, *Eur. J. Inorg. Chem.* **2008**, 1693.

[31] a) A. Panja, P. Guionneau, *Dalton Trans.* **2013**, *42*, 5068; b) A. Panja, M. Shyamal, A. Saha, T. K. Mandal, *Dalton Trans.* **2014**, *43*, 5443.

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