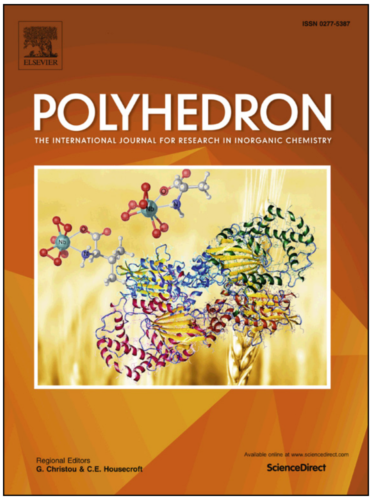

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Mixed valence trinuclear cobalt (II/III) complexes: Synthesis, structural characterization and phenoxazinone synthase activity

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ABSTRACT

Three new mixed valence trinuclear Co(II/III) compounds $[Co_3L_2(\mu_2–C_6H_5CO_2^-)_2(CH_3CN)_2](ClO_4^-)_2·(CH_3CN)_3$ (**1**) $[Co_3L^R_2(\mu_2–C_6H_5CO_2^-)_2(C_6H_5CO_2^-)_2]·(CH_3CN)_2$ (**2**) and $[Co_3L^R_2(\mu_2–C_6H_5CH{=}CH–CO_2^-)_2(C_6H_5CH{=}CH–CO_2^-)_2]·(CH_3)_2CO$ (**3**) have been synthesized by reacting the di-Schiff base ligand $[H_2L]$ or its reduced analogue $[H_2L^R]$ (where H_2L = N,N′-bis(salicylidene)-1,3-propanediamine) and (H_2L^R = N,N′-bis(2-hydroxybenzyl)-1,3-propanediamine) with cobalt perchlorate hexahydrate and sodium benzoate or sodium cinnamate. The complexes have been characterized by IR, UV-Vis and single crystal X-ray diffraction analyses. All the complexes are linear trinuclear species $[Co^{III}–Co^{II}–Co^{III}]$ in which two terminal octahedral $Co^{III}N_2O_2$ cores coordinate to the central octahedral Co^{II} ion through μ_2-phenoxido oxygen atom and the bridging carboxylato ions. In addition, the complexes (**2** and **3**) derived from reduced Schiff base ligand have, rather unusually, a terminally coordinated carboxylato ion to Co^{III}, which is acetonitrile molecule in case of complex (**1**) with unreduced ligand. Complex **2** has been found to be an excellent functional model for the phenoxazinone synthase activity, in the aerial oxidation of 2-aminophenol to the corresponding 2-aminophenoxazine-3-one chromophore in acetonitrile solvent medium. Detailed kinetic data analysis of this oxidation reaction reveals a fairly high phenoxazinone synthase activity of **2** with k_{cat} = 153.60 h^{-1}.

Keywords: Reduced Schiff base, Mixed valence cobalt (II/III), Phenoxazinone synthase.

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1. Introduction

The synthesis of cobalt Schiff base complexes is of continual interest due to their important structural variations [1], various catalytic activities [2], intriguing magnetic properties [3] and a wide range of medicinal applications [4]. The oxidation state of cobalt in these complexes in most cases is either +3 or +2 depending upon the nature of the Schiff bases and methods of syntheses. Besides, a few mixed valence (+3/+2) dinuclear species [5], trinuclear [6] and tetranuclear [7] cobalt Schiff base complexes are also reported in the literature. Among them, the trinuclear complexes deserve special attention as they can be derived easily from the salen type di-Schiff base ligands [8]. The common structural feature of these trinuclear complexes is that a central Co^{II} ion is connected with two terminal Co^{III} ions through double phenoxido bridges along with an additional anionic bridge (carboxylato [8,9] or chloride [10] or sulphito [11] or azido [6,12]) between the terminal and central cobalt atoms. It is also intriguing to note that the complexes derived from the di-Schiff base ligand of 1,2-ethanediammine are invariably mixed valence [Co^{III}–Co^{II}–Co^{III}] [8,9] but those of 1,3-propanediammine can be either mixed valence [Co^{III}–Co^{II}–Co^{III}] [13] or only divalent [Co^{II}–Co^{II}–Co^{II}] [14]. Recently, we observed interesting structural features in a mixed valence cobalt complex of a reduced Schiff base ligand, where the azido ion formed a bridge ($\mu_{1,3}$-N_3) between the two terminal Co(III) centers and participated in pnicogen bonding interactions [6]. The increased flexibility of less constrained –CH_2–NH– moiety of the reduced Schiff base compared to unreduced one and the presence of H-atoms onto the reduced nitrogens seemed to be responsible for such exceptional phenomena. To have comprehensive knowledge in the structural variations of such complexes, we are interested in synthesizing some more cobalt complexes using di-Schiff ligands and their reduced analogues.

The phenoxazinone synthase is a multicopper oxidase enzyme [15,16]. It is found naturally in the bacterium *Streptomyces antibioticus* and known to catalyze the oxidative coupling of 2-aminophenol to the phenoxazinone chromophore at the final step for the biosynthesis of actinomycin D [17]. This is medicinally used for the treatment of different type of tumors [18]. Therefore, the synthesis and characterization of functional model complexes for metalloenzymes that imitate this oxidase activity, is of great significance in the field of catalysis for the oxidation reactions [19]. Literature survey shows that some Co(II) [20] or Co(III) [20b,21] Schiff base complexes can mimic phenoxazinone synthase activity like complexes of Cu(II) [22] and Mn(II/III/IV) [23]. However, all the cobalt-Schiff base complexes which are known to exhibit this catalytic activity are mononuclear or dinuclear in which the cobalt ion is either in +2 or in +3 oxidation state [20,21]; till date, no mixed valence trinuclear cobalt complex is reported as functional model for this activity.

In this present report, we have synthesized and structurally characterized three trinucler mixed valence cobalt complexes, $[Co_3L_2(\mu_2{-}C_6H_5CO_2^-)_2(CH_3CN)_2](ClO_4^-)_2\cdot(CH_3CN)_3$ (**1**) $[Co_3L^R_2(\mu_2{-}C_6H_5CO_2^-)_2(C_6H_5CO_2^-)_2]\cdot(CH_3CN)_2$ (**2**) and $[Co_3L^R_2(\mu_2{-}C_6H_5CH{=}CH{-}CO_2^-)_2(C_6H_5CH{=}CH{-}CO_2^-)_2]\cdot(CH_3)_2CO$ (**3**) using Schiff base ligand, H_2L (where H_2L = N,N'-bis(salicylidene)-1,3-propanediamine) and its reduced form [H_2L^R] (where H_2L^R = N,N'-bis(2-hydroxybenzyl)-1,3-propanediamine) and carboxylato coligands (benzoato for **1** and **2**; cinnamato for **3**). Among them, only complex **2** exhibit phenoxazinone synthase activity. The detailed kinetic study reveals that the turnover number (k_{cat} = 153.60 h^{-1}) for this oxidase activity is significantly higher than similar reported complexes. Thus, complex **2** is the first example of mixed valence trinuclear cobalt complex showing rather high phenoxazinone synthase activity.

2. Experimental

2.1. Starting Materials

Salicylaldehyde, 1,3-propanediamine and sodium borohydride were purchased from Lancaster and were of reagent grade. They were used without further purification.

Caution! *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.*

2.2. Synthesis of the Schiff Base Ligand, N,N'-bis(salicylidene)-1,3-propanediamine (H_2L)

The Schiff base ligand was synthesized by a standard method [24]. 5 mmol of 1,3-propanediamine (0.42 mL) was mixed with 10 mmol of the salicylaldehyde (1.04 mL) in methanol (30 mL). The resulting solution was refluxed for *ca.* 2 h and allowed to cool.

2.3. Synthesis of the reduced Schiff base ligand, N,N'-bis(2-hydroxybenzyl)-1,3-propanediamine (H_2L^R)

The di-Schiff base ligand (H_2L) was synthesized as stated above. Then 30 mL (5 mmol) of this prepared methanolic ligand solution (H_2L) was cooled to 0°C, and solid sodium borohydride (570 mg, 15 mmol) was added to this methanolic solution with stirring. After completion of addition, the resulting solution was acidified with concentrated HCl (10 mL) and then evaporated to dryness on a hot water bath [25]. The reduced Schiff base ligand (H_2L^R) was extracted from the solid mass with methanol and this methanol solution (*ca*. 30 mL) was used for complex formation.

2.4. Synthesis of the complex $[Co_3L_2(\mu_2\text{–}C_6H_5CO_2^{-})_2(CH_3CN)_2](ClO_4^{-})_2\cdot(CH_3CN)_3$ *(**1**)*

The yellow coloured methanolic solution (12 mL) of the di-Schiff base (H_2L) ligand (2 mmol) was taken in a beaker. To this methanolic solution, a water solution (2 mL) of $Co(ClO_4)_2\cdot6H_2O$ (1.098 g, 3 mmol) followed by an aqueous solution (2 mL) of sodium benzoate (0.576 g, 4 mmol) was added. The mixture was stirred for 1 h and then filtered. The filtrate was allowed to stand overnight till brown coloured microcrystalline product of **1** appeared at the bottom of the beaker. The crystalline product was recrystallized from acetonitrile solution. The crystals were washed with an acetonitrile–water mixture and dried in a desiccator containing anhydrous $CaCl_2$ and then characterized by elemental analysis, spectroscopic methods, and X-ray diffraction.

Complex **1**. Yield: 0.917 g, 67%. Anal. Calc. for $C_{58}H_{57}Co_3Cl_2N_9O_{16}$: C 50.34, H 4.15, N 9.11; found: C 50.52, H 4.35, N 9.31%; UV/vis: [λ_{max} in nm (ε_{max} in M^{-1} cm^{-1})] (MeCN) = 621(223), 362(2908). IR (KBr) in cm^{-1}: ν(C=N) 1633; ν(C=O) 1597; ν(C=O) 1558.

2.5. Synthesis of the complexes $[Co_3L^R_2(\mu_2\text{–}C_6H_5CO_2^{-})_2(C_6H_5CO_2^{-})_2]\cdot(CH_3CN)_2$ *(**2**) and* $[Co_3L^R_2(\mu_2\text{–}C_6H_5CH{=}CH\text{–}CO_2^{-})_2(C_6H_5CH{=}CH\text{–}CO_2^{-})_2]\cdot(CH_3)_2CO$ *(**3**)*

Complexes **2** and **3** were prepared using the reduced Schiff base ligand with the same molar ratios of reactants as used for **1**, but here only in one case sodium cinnamate (4 mmol, 0.680 g) was used for the synthesis complex **3** instead of using sodium benzoate. The microcrystalline compound of **3** was recrystallized from acetone solution instead of acetonitrile.

Complex **2**. Yield: 0.734 g, 56%. Anal. Calc. for $C_{66}H_{66}Co_3N_6O_{12}$: C 55.53, H 4.62, N 7.31; found: C 55.72, H 4.83, N 7.37%; UV/vis: [λ_{max} in nm (ε_{max} in M^{-1} cm^{-1})] (MeCN) = 625(611), 374(2990), and 421(2698). IR (KBr) in cm^{-1}: ν(N-H) 3211; ν(C=O) 1698; ν(C=O) 1600.

Complex **3**. Yield: 0.841 g, 58%. Anal. Calc. for $C_{76}H_{80}Co_3N_4O_{14}$: C 62.94, H 5.56, N 3.86; found: C 62.82, H 5.42, N 3.76 %; UV/vis: [λ_{max} in nm (ε_{max} in M^{-1} cm^{-1})] (MeCN) = 620(637), 367(3715), and 419(3156). IR (KBr) in cm^{-1}: IR (KBr) in cm^{-1}: ν(N-H) 3245; ν(C=O) 1637; ν(C=O) 1597.

2.6. Physical Measurements

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 2400 series II CHN analyzer. IR spectra in KBr pellets (4000−400 cm^{-1}) were recorded using a Perkin- Elmer RXI FT-IR spectrophotometer. Electronic spectra in acetonitrile (800−200 nm) were recorded in a Hitachi U-3501 spectrophotometer.

2.7. ESI-HRMS

Electrospray ionization mass spectrometry (ESI-MS positive) ion mass spectra were acquired using a Xevo G2-S QTof (Waters) mass spectrometer, equipped with a Z-spray interface, over a mass range of 100–1200 Da, in a continuum mode. Aqueous sodium formate was used for Q-oa-Tof calibration. L-Leucine was used as the external mass calibrant lock mass $[M+H]^+$ = 556.2771 Da. The solution of compound **2** was injected at the flow rate of 5μl/min. The solution was made in mass-spectrometric grade acetonitrile. The concentrations of complex **2** as well as complexes + substrates in solutions were the same (10^{-5} M) during acquisitions of mass spectra.

2.8. Crystallographic data collection and refinement

Well formed single crystals of each compound had been mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo Kα (λ = 0.71073 Å) radiation. The crystals were located at 60 mm from the CCD, and frames (360) were measured with a counting time of 10 s. The structures were solved using the Patterson method through the SHELXS 97 program. Non hydrogen atoms were refined with independent anisotropic displacement parameters, while difference Fourier synthesis and least-squares refinement showed the positions of any remaining non-hydrogen atoms. The hydrogen atoms bound to carbon atoms were included in geometric positions and set thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Hydrogen atoms that bonded to N or O were placed in a difference Fourier map and refined with distance constraints. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least-squares refinement. All the acetonitrile solvent molecules outside the coordination sphere are refined isotropically using distance constraints with 50% occupancy for structures, **1** and **2**. In addition, for structure **1**, the perchlorate oxygen atoms were disordered and refined isotropically using distance constraints with 50% occupancy of each O-atom. Absorption corrections were carried out using the SADABS program [26], while all calculations were made *via* SHELXS 97 [27], SHELXL 97 [28], PLATON 99 [29], ORTEP-32 [30], and WINGX system ver-1.64 [31] and refined using SHELXL-2014 [31]. Data collection, structure refinement parameters, and crystallographic data for all three complexes are given in Table S1.

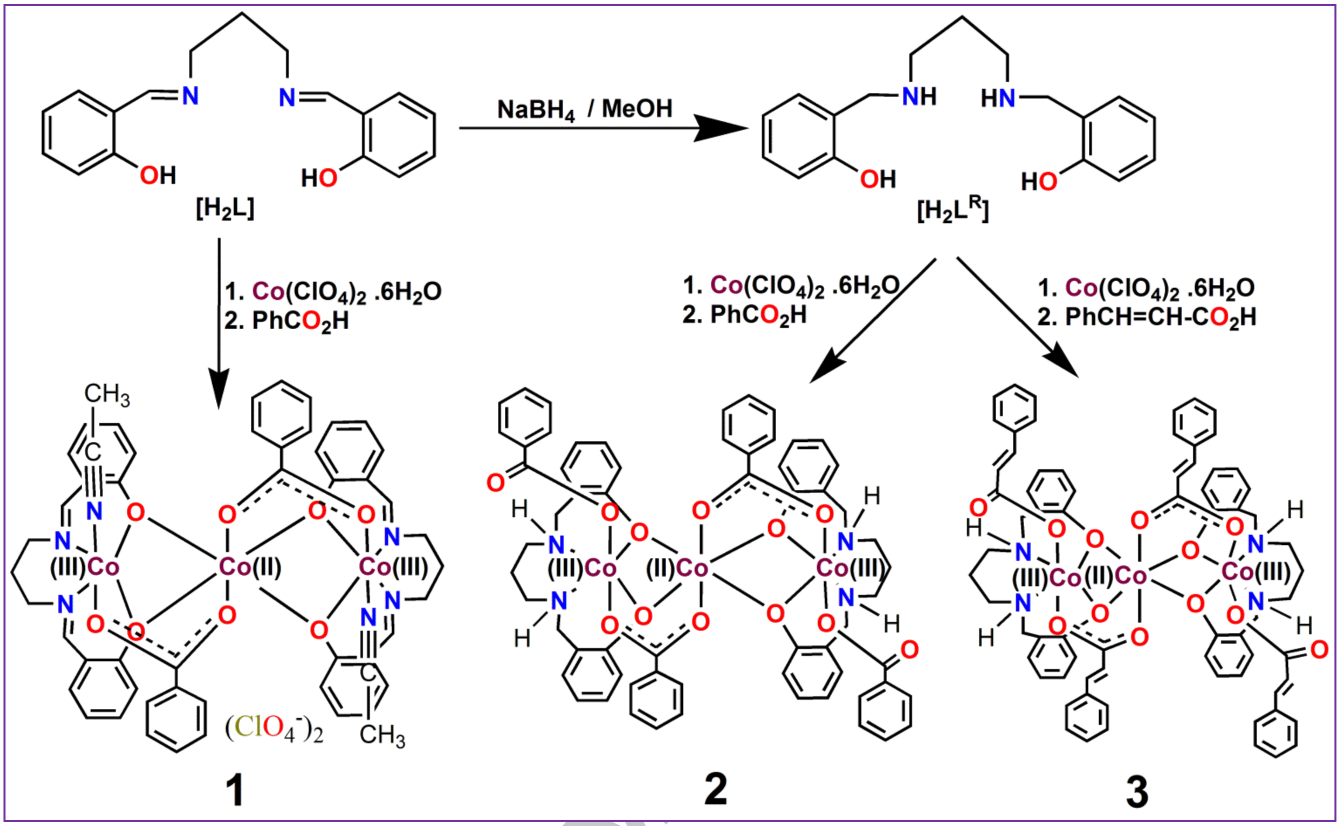
2.9. Oxidation of 2-aminophenol

In order to study the phenoxazinone synthase activity of **1**-**3**, a 10^{-4} (M) solution of each complex in acetonitrile was treated with 100 equiv of 2-aminophenol (OAPH) dissolved in acetonitrile under aerobic conditions at room temperature. Absorbance *vs* wavelength (wavelength scan) of these solutions was recorded at a regular time interval of 5 min in the wavelength range 300−500 nm for all complexes. Amongst, only complex **2** showed this activity. To determine the dependence of rate on substrate concentration and various kinetic parameters, a 10^{-4} M solution of complex **2** was treated with 10, 30, 50, 70, and 100 equiv of substrate. The reactions were followed spectrophotometrically by monitoring the increase in the maximum absorbance of the phenoxazinone band at 432 nm as a function of time (time scan).

3. Results and Discussion

3.1. Syntheses of the Complexes

The Schiff-base ligand (H_2L) and its reduced analouge (H_2L^R) were synthesized using the reported procedures. These ligands (H_2L or H_2L^R) on reaction with cobalt(II) perchlorate hexahydrate and sodium benzoate or sodium cinnamate in 2:3:4 molar ratios in MeOH-H_2O medium (10:1, v/v) resulted in three new trinuclear mixed valence Co(II/III) complexes, $[Co_3L_2(\mu_2{-}C_6H_5CO_2^-)_2(CH_3CN)_2](ClO_4^-)_2\cdot(CH_3CN)_3$ (**1**) $[Co_3L^R{}_2(\mu_2{-}C_6H_5CO_2^-)_2(C_6H_5CO_2^-)_2]\cdot(CH_3CN)_2$ (**2**) and $[Co_3L^R{}_2(\mu_2{-}C_6H_5CH{=}CH{-}CO_2^-)_2(C_6H_5CH{=}CH{-}CO_2^-)_2]\cdot(CH_3)_2CO$ (**3**) (Scheme 1).



Scheme 1. Synthesis of complexes **1**–**3**.

3.2. IR and UV−Vis Spectra

Besides elemental analyses, all three complexes were initially characterized by the IR spectra. A strong and sharp band due to the azomethine ν(C=N) group of the Schiff base appears at 1633 cm^{-1} for the complex **1** (Fig. S1). On the other hand, a moderately strong peak at a range of 3210-3245 cm^{-1} (due to a N–H stretching vibration) for complexes **2** and **3** (Figs. S2 and S3) indicates that the imine group of the Schiff base is reduced [32]. In addition, the presence of carboxylato ligands in all three complexes are confirmed by the appearance of strong and sharp peaks at 1597, 1698, and 1637 cm^{-1} along with shoulders at 1558, 1600 and 1597 cm^{-1} in the spectra of **1**-**3**, respectively (Figs. S1–S3). The splitting of the band is indicative of the presence of two different types (symmetric and asymmetric) of stretching vibration of carboxylato coligands in each case.

The electronic spectra of the compounds were recorded in acetonitrile solutions. The complexes show a broad absorption band in the visible region at 621, 625 and 620 nm in acetonitrile solution for **1**-**3** respectively, attributed to d−d transitions of Co(II) ions. Besides these bands, an absorption band in the range 362−421 nm was observed in acetonitrile solution assignable to ligand-to-metal charge transfer transitions for all the complexes (Figs. S4−S5).

3.3. Description of Structures

*3.3.1. Complex **1***

The linear trinuclear structure of **1** having molecular formula $[Co_3L_2(\mu_2\text{–}C_6H_5CO_2^{-})_2(CH_3CN)_2](ClO_4^{-})_2\cdot(CH_3CN)_3$ is shown in Fig. 1 together with the atomic numbering scheme. Dimensions of the metal coordination sphere of **1** are given in Table S1 in the Supporting Information. The structure contains a crystallographic inversion center (symmetry: 2-x, -y, 2-z), which sits on the central cobalt atom [Co(2)]. Thus, the asymmetric unit consists of two metal centers [Co(III)-terminal and Co(II)-central], one deprotonated di-Schiff base ligand $[(L)^{2-}]$, one benzoate co-anion and one perchlorate anion. The basal plane of the terminal Co(III) center is formed by two μ_2-phenoxido O atoms and two imine N atoms of the chelated dianionic tetradentate Schiff-base ligand $[L^{2-}]$ and the axial positions are occupied by one oxygen atom of benzoate anion and one nitrogen from acetonitrile solvent molecule. The basal Co–O bond distances [1.898(4)–1.912(4) Å] are shorter than the basal Co–N bond distances [1.922(6)–1.960(5) Å] (Table S2). The four donor atoms in the basal plane show root mean square (r.m.s) deviations of 0.009 Å for Co(1) with the metal atom 0.001(1) Å shifted from the mean plane towards the axially coordinated nitrogen atom. The dihedral angle between two N–Co–O planes [0.78(21)°] and the ranges of *trans* [172.8(2)–176.8(2)°] and *cis* [83.3(2)–95.6(2)°] angles (Table S2) around Co(1) suggested a distort octahedral geometry of the terminal cobalt center.

The central cobalt atom is bonded to four oxygen atoms from the two ligands $[(L)^{2-}]$, which form the basal plane of the Co(II), while the trans axial positions are occupied by the two oxygen atom from benzoate anions.

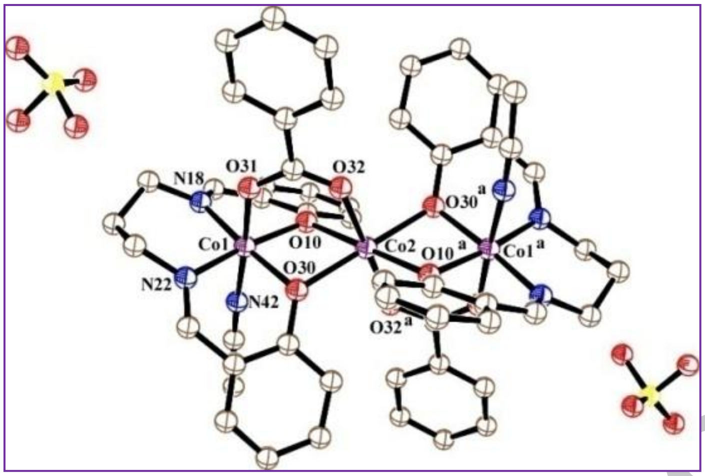


Fig. 1. The structure of **1** with ellipsoids at 30% probability. H-atoms are removed for clarity. The solvent acetonitrile molecules are also omitted for clarity. Symmetry element ^{a} = 2-x, -y, 2-z.

All the central Co–O bond distances [2.030(4)–2.089(4) Å] are considerably greater than that of the terminal cobalt centers [1.893(4)–1.912(4) Å] as the central cobalt atom is in +2 oxidation state whereas the terminal atoms are in +3 oxidation states. The range of *cis* angles [75.0(2)–85.8(2)°] around this central Co center is an indicative of a distortion from its ideal octahedral geometry. The Co(1)···Co(2) distance is 3.030(1) Å.

*3.3.2. Complexes **2** and **3***

Partially labeled diagrams of trinuclear structures of **2** and **3** are depicted in Figs. 2 and 3 respectively, and selected bond parameters are summarized in Table S2. Both structures (**2** and **3**) contain three cobalt atoms [Co^{III}–Co^{II}–Co^{III}] in a perfect linear arrangement, owing to the presence of a crystallographic inversion center (symmetry: 2-x, -y, 2-z and 1-x, 1-y, 1-z for **2** and **3**, respectively) at the central metal atom Co(2). In each of the structures (**2** and **3**) every cobalt atom has a six-coordinated octahedral geometry like **1**. The basal plane of the two terminal Co(III) centers of each structure is formed by two μ_2- phenoxido O atoms and two imine N atoms of the dianionic tetradentate reduced Schiff-base ligand [$(L^{2-})^{R}$] but unlike **1,** the axial positions are occupied by two oxygen atoms from one bridging and another terminal carboxylato ions [benzoato and cinnamato for **2** and **3,** respectively]. The r.m.s deviations of the four basal atoms for Co(1) are 0.033 and 0.018 Å and these are 0.001(1) and 0.021(1) Å shifted from the mean plane for **2** and **3**, respectively. The basal Co–O bond distances of the terminal cobalt are shorter than the basal Co–N bond distances (Table S2) like **1**. It is noticeable that all the terminal Co–

O/N bond distances are longer for **2** and **3** compared to those of **1**. The ranges of *trans* [173.3(3)–176.6(3)° for **2** and 172.9(2)–176.0(2)° for **3**] and *cis* [81.0(2)–95.8(3)° for **2** and 81.3(2)–95.5(2)° for **3**] angles (Table S2) indicate a slight deviation from the ideal octahedral geometry of the terminal cobalt centers like **1**. The dihedral angle between two N–Co–O planes for **2** and **3** (2.79(23)º and 2.16(19)º, respectively) are considerably greater compared to that of complex **1**.

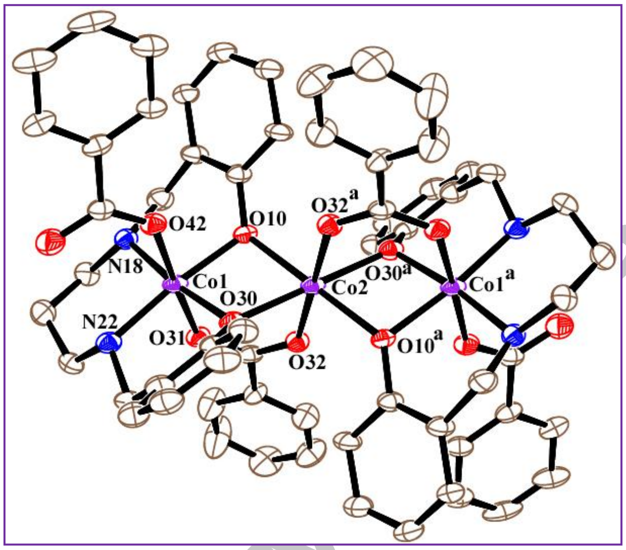


Fig. 2. The structure of **2** with ellipsoids at 30% probability. H-atoms are removed for clarity. The solvent acetonitrile molecules are also omitted for clarity. Symmetry element ^{a} = 2-x, -y, 2-z.

The central Co(II) atom in each case (**2** and **3**) is bonded to four phenoxido oxygen atoms of deprotonated tetradentate reduced Schiff base ligands and two oxygen atoms from the two bridging carboxylate ions like **1**. Here, all Co(II)–O bond distances are almost same (Table S2) range like **1**. Again, here also the central Co–O bond distances are significantly greater than that of the terminal cobalt centers just like **1** (Table S2). The central cobalt atom [Co(2)] presents a six-coordinated slightly distorted octahedral geometry and this is confirmed by the range of *cis* angles [75.6(2)–84.5(2)° for **2** and 74.6(1)–84.7(2)º for **3**]. The Co(2)···Co(1) distances are 3.055(1) and 3.045(3) Å for **2** and **3**, respectively.

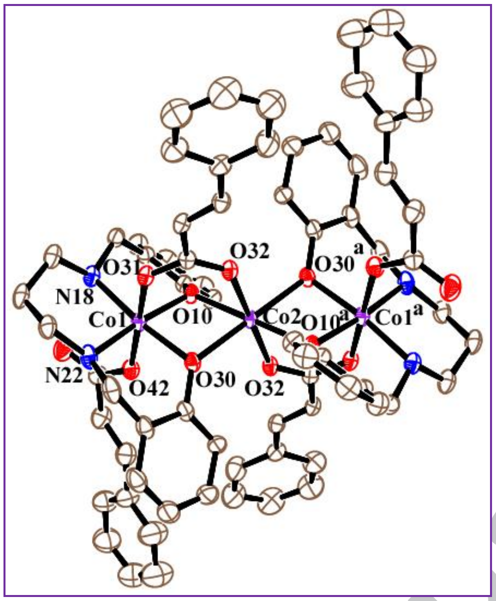


Fig. 3. The structure of **3** with ellipsoids at 30% probability. H-atoms and the solvent acetone molecules are also omitted for clarity. Symmetry element ^{a} = 1-x, 1-y, 1-z.

Both structures (**2** and **3**) contain an intramolcular H-bonding between the O atom [O43] of the terminal carboxylao ligand and the hydrogen atoms (H18 and H22) of the reduced imine moiety [N(18)–H(18)···O(43) and N(22)–H(22)···O(43) with dimensions H18···O43 2.927(77) and 1.818(23) Å, H22···O43 2.014(31) and 3.111(45) Å, N18–H18···O43 116.2(36)° and 173.6(21)°, N22–H22···O43 143.8(27)° and 113.2(18)° for **2** and **3**, respectively (Table S3)] [Fig. 4].

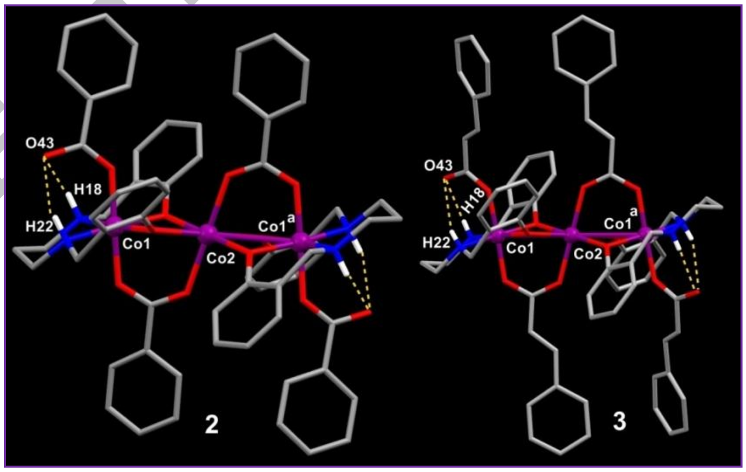
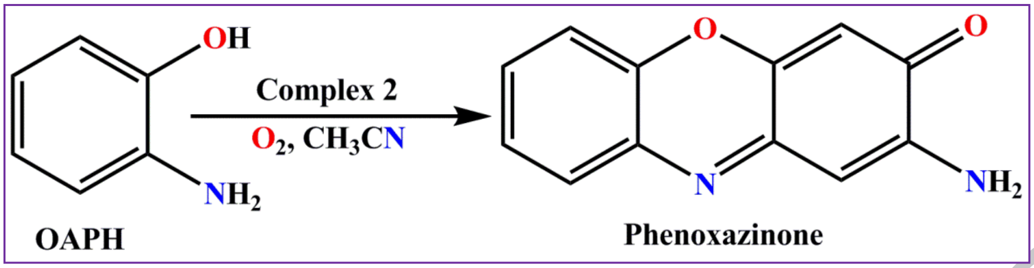


Fig. 4. The hydrogen bonding interaction (O43···H22/H18–N22/N18) in the structures of **2** and **3**. Symmetry element ^{a} = 2-x, -y, 2-z and ^{a} = 1-x, 1-y, 1-z for **2** and **3**, respectively.

A CSD search for trinuclear Co^{III}–Co^{II}–Co^{III} complexes containing a deprotonated tetradentate Schiff base ligand reveals that twelve such structures have been reported so far [8-13]. Among them, eight complexes are linear in which the terminal Co(III) and the central Co(II) are linked through acetato (six structures) [8,9,13] or sulfito (one structure) [11] or chlorido (one structure) [10] bridges in addition to double phenoxido bridges. The remaining four are azido bridged angular trinuclear species [6,12]. In case of the structures with acetato bridges (six examples), the remaining axial position of the octahedral terminal metal center is coordinated to another coligand. Four of these structures are derived from 1,2-ethanediammine based Schiff bases where terminal coligand is acetato in three [8,9a] and thiocyanato in the other one [9b]. The terminal coligand is pyridine [13b] or thiocyanato [13a] in the two structures derived from 1,3-propanediammine based Schiff base ligand. It has been argued that crystal field stabilization energy of the carboxylate ion is not strong enough to stabilize the terminal Co ion in +3 oxidation state in case of Schiff base derived from 1,3-propanediammine due its longer bond distances compared to those derived from 1,2-ethanediammine. Hence there is no structure in which carboxylato ion is coordinated to the terminal Co(III) ion and the Schiff base is derived from 1,3-propanediammine. However, stronger CFSE of pyridine or thiocyanate ligand is assumed to be crucial in the stabilization of the two structures with 1,3-propanediammine. In the present study, structures **2** and **3** are the first examples in which terminal coordination mode of carboxylato ion is observed in Co(III) with 1,3-propanediammne based Schiff base ligand. The strong hydrogen bonding interaction (Fig. 4) between non coordinated carboxylato O-atom and H-atom onto the reduced nitrogen seems to be responsible for stabilization of these two structures (**2** and **3**).

3.4. Phenoxazinone synthase activity studies with kinetics

The phenoxazinone synthase activity of the complexes for the oxidation of 2-aminophenol (OAPH) to 2-aminophenoxazine-3-one in aerobic condition according to the reaction shown in Scheme 2 was evaluated spectrophotometrically in acetonitrile solution at room temperature. The oxidation product, phenoxazinone is highly stable and has characteristic absorption band maxima at around 432 nm in a pure acetonitrile solvent. Before going into the details of kinetics studies, we examined the catalytic activity of all three complexes for the oxidation of 2-aminophenol in acetonitrile solvent.



Scheme 2. Catalytic oxidation of OAPH to 2-aminophenoxazine-3-one in an acetonitrile solvent.

For this purpose, (1 x 10^{-4}) M acetonitrile solution of the complexes (**1-3**) were reacted with 100 equivalents of substrate OAPH at room temperature under aerobic condition. After addition of the substrate (OAPH) into the complexes, the progress of the reaction was followed by recording the UV−vis spectrum of the said mixture at 5 min times interval. The gradual increase of an absorption band around 432 nm was observed in UV−vis spectroscopy only for complex **2**, but not for complexes **1** and **3**. This indicates that only complex **2** catalyzes the aerobic oxidation of OAPH to 2-aminophenoxazine-3-one. Hence, the detailed kinetic studies have been performed only on complex **2**. The variation of the spectral behavior after the addition of OAPH in the complex **2** for the period of 1.5 h is shown in Fig. 5.

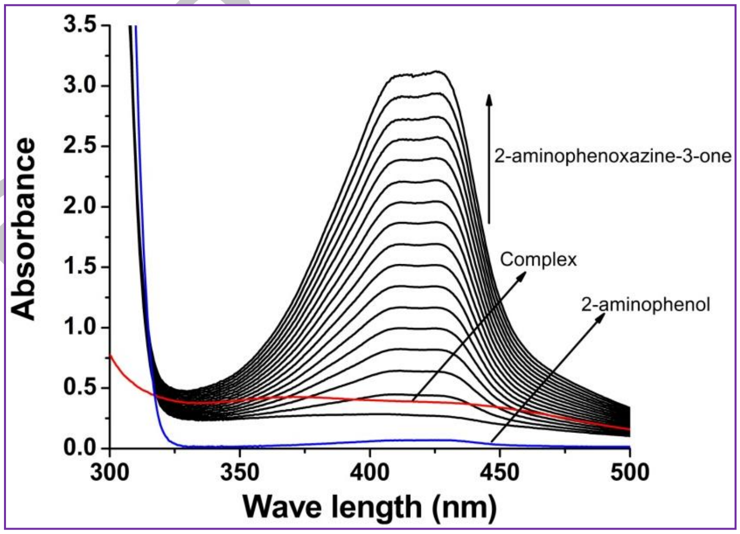


Fig. 5. Increase of the phenoxazinone band at around 432 nm after the addition of 100 equiv. of OAPH to an acetonitrile solution of complex **2**. The spectra were recorded at 5 min intervals.

The kinetics of the oxidation of OAPH to 2-aminophenoxazine-3-one by the complex **2** was determined by the method of initial rates by monitoring the development of the phenoxazinone band at 432 nm as a function of time. To maintain pseudo-first-order kinetics, the substrate (OAPH) concentration was always set at least 10 times higher than that of the complex **2**. The rate constant for a particular complex–substrate mixture was determined from the log [Aα/(Aα − At)] *vs*. time plot. The oxidation rates and various kinetic parameters of the substrate concentration were determined by using (1×10^{-4}) M solutions of **2** with different concentrations (From 1×10^{-2} M to 0.1×10^{-2} M) of OAPH under aerobic conditions. In this kinetic study, at lower concentration of OAPH the first-order kinetic was observed, whereas saturation kinetics resulted in higher concentration. This observation pointing out that the oxidation of OAPH passes through a relatively stable complex–substrate intermediate adduct, most probably formed by the coordination of substrate to catalyst by the replacement of a terminal benzoate ion (Figs. S6 and S7). The observed rates *versus* the concentration of substrate data were then analyzed on the basis of the Michaelis–Menten approach of enzymatic kinetics to obtain the Lineweaver–Burk (double reciprocal) plot and values of kinetic parameters *e.g.* V_{max}, K_M, and k_{cat}. Both the curves of the observed rate *vs*. [substrate] and the Lineweaver–Burk plot for complex **2** are shown in Fig. 6.

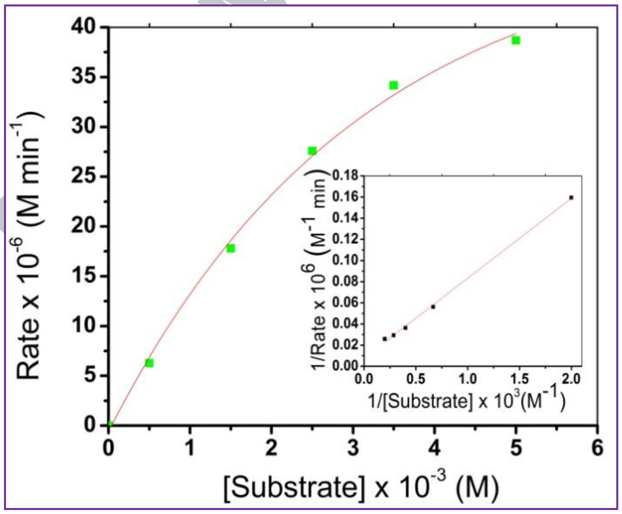


Fig. 6. Plot of the rate *vs* substrate concentration for complex **2**. Inset shows the corresponding Lineweaver–Burk plot.

The kinetic parameter for the complex **2** is listed in Table 1. The k_{cat} value can be calculated by dividing the V_{max} value by the concentration of the complex (Table 1). The k_{cat} (in h^{-1}) value is

153.60 for **2**. This value lies in the higher range of the k_{cat} values of the cobalt Schiff Base complexes behaving as functional models of phenoxazinone synthase [see Table 2].

To get a better understanding of the complex–substrate intermediate of phenoxazinone synthase activity during the oxidation reaction, we have recorded ESI-MS spectra for complex **2**, and a 1:10 mixture of the complex to and OAPH within 10 min of mixing in acetonitrile solvent (Figs. S6 and S7, Supporting Information). Complex **2** shows the base peak at m/z = 431.9913 (calcd 432.0294) which can be assigned to the dinuclear species $[Co_2(L^R\text{-}2H)(MeOH)]^+$. In addition, peaks due to the other dinuclear $[Co_2(L^R\text{-}2H)]^+$, $[Co_2(L^R\text{-}H)(C_6H_5CO_2)]^+$ and trinuclear $[Co_3(L^R\text{-}H)_2(C_6H_5CO_2)]^+$, $[Co_3(L^R)_2(C_6H_5CO_2)_3]^+$ species at m/z = 400.00 (calcd 400.0032), 522.04 (calcd 522.0400) and 864.1172 (calcd 864.1179), 1108.19 (calcd 1108.1914), respectively are also observed for complex **2**. After the addition of OAPH to the solutions of complex **2**, drastic changes are observed. In addition to the protonated 2-aminophenoxazine-3-one $[C_{12}H_{11}N_2O_2]^+$ base peak at 215.08 (calcd 215.0821), a new peak appears at m/z = 509.05 (calcd 509.0560) which corresponds to the coordination of OAPH to the dinuclear species $[Co_2(L^R\text{-}H)(OAPH)]^+$. These results reveal the formation of the catalyst–substrate as intermediates which take part in substrate activation during the oxidation of OAPH to 2-aminophenoxazine-3-one.

Thus, this mixed valence Co(III)–Co(II)–Co(III) compound can be considered as a functional model of phenoxazinone synthase activity. It is important to mention that the k_{cat} value obtained for complex (**2**) is considerably higher than most of those reported for mononuclear or dinuclear cobalt compounds in which the cobalt ion is either in +2 or in +3 oxidation state. Therefore, complex **2** is not only the first example of mixed valence trinuclear cobalt Schiff base complex exhibiting this phenoxazinone synthase activity but its k_{cat} value is one of the highest among the reported Co(II) or Co(III) compounds (Table 2).

Detailed investigations with copper or cobalt based model complexes of phenoxazinone synthase activity have shown that various factors may affect their catalytic activity, such as the metal−metal distance, ligand flexibility, exogenous bridging ligand, and coordination geometry around the metal center [19-22]. Among the Co(III)/Co(II) mixed valence compounds reported herein, phenoxazinone synthase activity is observed only for **2**, whereas **1** and **3** are inactive towards OAPH oxidation. In case of complex **3**, perhaps the extra π electron conjugation in exogenous cinnamato ligand makes it weaker leaving group in comparison to benzoato in **2** (pKa

= 4.46 and 4.20 at 25ºC for cinnamic acid and benzoic acid, respectively) and consequently binding of the substrate (OAPH) to the metal center is restricted for **3**. However, in the same light of explanation complex **1** should show this activity but it is inactive and this is may be due to the relatively less conformational flexibility on the unreduced Schiff base moiety (-C=N-) and absence of any terminal benzoate ion. In addition, although there is a terminal acetonitrile solvent molecule in **1** but may be due to strong coordination of acetonitrile molcule to the terminal Co(III) at a distance 1.899(2)Å prevents the substitution of acetonitrile molecule by the substrate OAPH. Therefore, the approach and coordination of the substrate to the metal center are more favorable in those cases where the flexible ligand is used for complexation and existence of easily removable exogenous coligand and these criteria are full filled in only complex **2** (supported from ESI-MS spectra, Figs. S6 and S7**)** and hence it is highly reactive to this catalytic activity.

4. Conclusion

In this present work, we synthesized three mixed valence [Co^{III}–Co^{II}–Co^{III}] trinuclear complexes using unreduced and reduced forms of N,N′-bis(salicylidene)-1,3-propanediamine and carboxylato ion. The unreduced ligand produces the usual linear trinuclear complex (**1**) in which two benzoate ions bridge the central and terminal cobalt atoms as reported before. However, in complexes (**2** and **3**) with the corresponding reduced Schiff base ligand two types of coordination mode of carboxylato ion are observed: one is bridging and other one is terminal. In these two structures the terminal coordination mode of carboxylato ion to the Co(III) centres seems to be stabilized through H-bonding interaction between carboxylato O-atom and H-atom onto the reduced nitrogen. Examination of phenoxazinone synthase activity for all three complexes reveals that only complex **2** catalyzes the oxidation of OAPH to the corresponding phenoxazinone derivative and it is the first example of mixed valence trinuclear cobalt complex that shows this catalytic activity with turnover number, k_{cat} = 153.60 h^{-1} which is significantly high compared to the reported Co(II) or Co(III) complexes.

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Appendix A. Supplementary data

CCDC 1529186−1529188 contains the supplementary crystallographic data for (**1**–**3**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data (IR spectra, UV–Vis spectra and mass spectrum (Figs. S1–S7) as well as tables for bond parameters (Tables S1 and S2) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2016.07.035.

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Table 1

Kinetic Parameters for the Oxidation of OAPH Catalyzed by Complex **2**.

Complex	V_{max} (M min^{-1})	Std. error	K_M (M)	Std. error	K_{cat} (h^{-1})
2	12.8 X 10^{-5}	2.47 X 10^{-5}	9.66 X 10^{-3}	1.98 X 10^{-4}	153.60

Table 2

k_{cat} Values for the oxidation of OAPH to 2-aminophenoxazine-3-one catalyzed by complex **2** and other reported cobalt complexes[a].

Complexes	k_{cat} (h^{-1}) in CH_3CN	k_{cat} (h^{-1}) in CH_3OH	References
$[Co^{III}(L^1)_3]$	Not done	Not calculated k_{cat}	21c
$[Co^{III}_2(L^2)_2(\mu\text{-}L^3)_2Cl_2]\ Cl_2\cdot 2H_2O$	Not done	13.75	21b
$[Co^{III}(L^4)(N_3)_3]$	Not done	20.37	21a

$[Co^{III}(L^5)(N_3)_3]$	Not done	33.26	21a
$[Co^{III}_2(L^6)_2(\mu\text{-}O_2)](ClO_4)_4\cdot 2CH_3CN$	Not done	30.09	20b
$[Co^{III}_2(L^7)_2(\mu\text{-}O_2)](ClO_4)_4$	Not done	23.04	20b
$[Co^{II}(L^8)(CH_3CN)](ClO_4)_2$	Not done	3.36	20b
$[Co^{II}(L^9)(H_2O)](ClO_4)_2$	Not done	6.37	20b
$[Co^{II}(L^{10})(H_2O)](ClO_4)_2$	Not done	8.28	20b
$[Co^{II}(L^{11})Cl(H_2O)]Cl.H_2O$	Not done	13.68	20a
$[Co^{II}(L^{11})(NCS)_2]$	Not done	7.38	20a
$[Co^{II}(L^{12})Cl_2]$	Not done	4.10	20a
$[Co^{III}(L^{13})(bzan)(N_3)]$	247.20	Not done	21d
$[Co^{III}(L^{13})(bzan)(NCS)]$	257.40	Not done	21d
$[Co^{III}(L^{14})(N3)(L^{15})]$	Not done	499.20	21e
$[Co^{III}(L^{16})(acna)(N_3)]$	77.52	Not done	21f
$[Co^{III}(L^{17})(bzan)(N_3)]$	77.12	Not done	21f
$[Co_3L^R{}_2(\mu_2\text{–}PhCO_2{}^-)_2(PhCO_2{}^-)_2]$	153.60	Not done	Present study

[a] Where L^1 = 4,4′-dimethyl-2,2’-bipyridine; L^2 = 2-aminomethylpyridine; L^3 = 2-iminomethylpyridine anion; L^4 = Bis-(2-pyridylmethyl)amine; L^5 = (2-pyridylmethyl)(2-pyridylethyl) amine; L^6 = N^1-(3-((pyridin-2-yl)methyleneamino)propyl)-N^3-((pyridin-2-yl)methylene)propane-1,3- diamine; L^7 = N^1-(3-(1-(pyridin-2-yl)ethylideneamino)propyl)-N^3-(1-(pyridin-2-yl)ethylidene)propane-1,3-diamine; L^8 = N^1-(3-(methoxy(6-methylpyridin-2-yl)methylamino)propyl)-N^3-((6-methylpyridin-2-yl)methylene)propane-1,3-diamine; L^9 = N^1-(3-((6-methylpyridin-2-yl)methyleneamino)propyl)-N^3-((6-methylpyridin-2-yl)methylene)propane-1,3-diamine; L^{10} = N^1-(3-((6-methylpyridin-2-yl)methyleneamino)propyl)-N^1-methyl-N^3-((6-methylpyridin-2-yl)methylene)propane-1,3-diamine; L^{11} = N,N’-bis(pyridin-2-ylmethylene)-2,2- dimethylpropane-1,3-diamine; L^{12} = N,N′-bis(6-methylpyridin- 2-ylmethylene)-2,2-dimethylpropane-1,3-diamine; HL^{13} = 2-(3-(dimethylamino)propyliminomethyl)-6-ethoxyphenol; Hbzan = 1-benzoylacetone; HL^{14} = 1-((2-(diethylamino)ethylimino)methyl)naphthalene-2-ol; HL^{15} = acetylacetone; HL^{16} = 2((2(2-hydroxyethylamino) ethylimino)methyl)-6-ethoxyphenol, Hacna = 2-acetyl-1-naphthol; HL^{17} = 1 ((2(diethylamino)ethylimino)methyl)naphthalen-2-ol.

Research highlights:

- Mixed valence Co(II/III) complexes derived from reduced salen-type Schiff base ligand.
- All three complexes with carboxylato coligand are linear structures $[Co^{III}–Co^{II}–Co^{III}]$.
- Complex **2** is the first example of mixed valence trinuclear cobalt complex with a high phenoxazinone synthase activity (k_{cat} = 153.60 h^{-1}).

Graphical Abstract (Pictogram)

Mixed valence trinuclear cobalt (II/III) complexes: Synthesis, structural characterization and phenoxazinone synthase activity

Alokesh Hazari,[a,b] Avijit Das[a], Prithwish Mahapatra[a], and Ashutosh Ghosh [a]*

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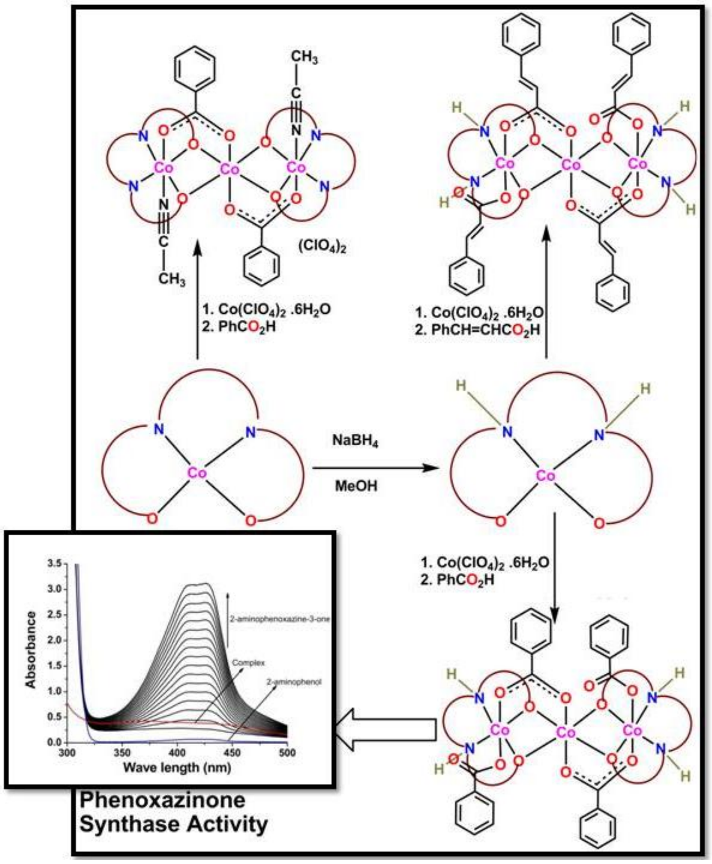

Graphical Abstract (Synopsis)

Mixed valence trinuclear cobalt (II/III) complexes: Synthesis, structural characterization and phenoxazinone synthase activity

Alokesh Hazari,[a,b] Avijit Das[a], Prithwish Mahapatra[a], and Ashutosh Ghosh [a]*

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Two of the three complexes are the first examples of the terminal coordination of carboxylato ion to Co(III) of a mixed valence Co^{III}-Co^{II}-Co^{III} complex with 1,3-propanediammine based Schiff base ligand and one shows phenoxazinone synthase activity with considerably high turnover number.