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Introduction

Dioxygen is known as ultimate "green" oxidant as it is atom economic and freely available in the environment. Transitionmetal active sites of proteins play vital roles in dioxygen binding and oxidation of a variety of important biological processes because they facilitate the spin-forbidden interaction between dioxygen and organic matter.^{1–3} Study of the model complexes of such metalloenzymes is therefore of great importance as those guides for the development of small molecule catalysts for specific oxidation reactions of organic substances in the industrial and synthetic processes. One of the major multicopper oxidase enzyme is phenoxazinone synthase,^{4,5} which is found naturally in the bacterium *Streptomyces antibioticus*. The function of this enzyme is to catalyze the oxidative coupling of two molecules of a substituted *o*-aminophenol

Postgraduate Department of Chemistry, Panskura Banamali College, Panskura RS, Purba Medinipur, West Bengal 721 152, India. E-mail: ampanja@yahoo.co.in †Electronic supplementary information (ESI) available: Fig. S1–S9, Scheme S1 and Table S1. CCDC 959180–959184 for complexes 1–5. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53546k

Exclusive selectivity of multidentate ligands independent on the oxidation state of cobalt: influence of steric hindrance on dioxygen binding and phenoxazinone synthase activity[†]

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The present report describes the syntheses, characterizations, crystal structures and study of the phenoxazinone synthase activity of two peroxo-bridged dicobalt(III) complexes, $[Co_2(L^1)_2(\mu-O_2)](ClO_4)_4$ ·2CH₃CN (1) and $[Co_2(L^2)_2(\mu-O_2)](ClO_4)_4$ (2), and three mononuclear cobalt(II) complexes, $[Co(L^3)(CH_3CN)](ClO_4)_2$ (3), $[Co(L^4)(H_2O)](ClO_4)_2$ (4) and $[Co(L^5)(H_2O)](ClO_4)_2$ (5), derived from the pentadentate ligands $L^1 - L^5$. which are the 1:2 condensation products of triamines and 2-acetylpyridine or 2-pyridinecarboxaldehyde (6-methyl-2-pyridinecarboxaldehyde). X-ray crystallography reveals exclusive selectivity of the acyclic Schiff dibasic form of the ligands over the heterocyclic analogues, and this selectivity is found to be insensitive to the oxidation state of cobalt. Other first row transition metals have been characterized in either form of the ligands in their complexes but it is specific for cobalt established in the present study. The pronounced effect of the methyl substitutions is observed from their crystal structures; substitution at imine-C does not have any significant influence on the peroxo-bridging but substitution at sixth position of pyridyl ring prevents the formation of peroxo-bridging, and both the steric and electronic factors play vital roles on such chemical diversity. All the complexes show the phenoxazinone synthase mimicking activity and the comparative catalytic activity has been explored. Although electrochemical behaviors of all the complexes are very similar, their relative catalytic activity mimicking the function of phenoxazinone synthase arises from the electronic and steric factors of the methyl substitution.

> (OAPH) to the phenoxazinone chromophore in the final step for the biosynthesis of actinomycin D.⁶ The later is one of the most potent antineoplastic agents known which inhibits DNAdependent RNA synthesis by intercalation of the phenoxazinone chromophore to DNA.^{7,8} Only a few functional models based on the transition-metal ions have been reported which show phenoxazinone synthase activity, and none of the reports dealt with structure–property correlation towards the phenoxazinone synthase mimicking activity.⁹⁻¹⁶ Therefore, the straightforward structure–property correlation for the phenoxazinone synthase is still lacking, indicating further that the problem of modeling the phenoxazinone synthase activity remains still open.

> A number of transition metal complexes with multidentate ligands derived from the condensation reaction of aromatic aldehydes with α,ω -di-primary polyamines have been extensively studied.^{17,18} Condensation reactions of such aldehydes with triamine that contains both the primary and secondary amines not only produce Schiff dibases, but also Schiff monobase with an additional saturated heterocyclic ring (imidazolidine or hexahydropyrimidine).¹⁹ Moreover, metal assisted isomerization among these products through formation or



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opening of the heterocyclic ring is quite common.^{20,21} Boča et al.²² have suggested that the Lewis acidity of the metal ion plays important role as it competes with the acidity of the -C=N- site, so that there is a delicate balance between $N^{\delta-}$ atom and C^{δ^+} center coming together (ring-closing of heterocycle) and going apart (ring-opening of heterocycle). The direction in which the system will shift depends on the relative acidity of imine-C and metal centers. Weak Lewis acids such as Fe²⁺, Co²⁺, and Cu²⁺ are incapable (or only partly capable) of opening the heterocyclic ring, while strong Lewis acids (e.g., Fe^{3+} and Zn^{2+}) can readily do so with the gain of the denticity of ligands. On the other hand, Tuchagues et al.¹⁹ pointed out that size of the metal ion plays deciding role in shifting the ligand equilibrium towards the tautomeric form most appropriate to each specific cation. Low-spin Fe²⁺ has a small enough ionic radius (75 pm) to stabilize the imine isomer in its complex, while the ionic radius of Ni²⁺ (83 pm) is probably too large for allowing coordination of the imine tautomer, and thus it stabilizes the cyclic analogue.

We have recently reported the study of the oxidation of o-aminophenol (OAPH) by some mononuclear cobalt(III) and a bis(imido)-bridged dinuclear cobalt(III) complexes in aerobic condition.²³⁻²⁵ These results suggested that the electronic environment around the metal centers along with the labile position in metal sites plays significant role for such activity. Our continuing interest in the bioinspired catalytic chemistry thus lead us to explore the reaction between 2-pyridinecarboxaldehyde (6-methyl-2-pyridinecarboxaldehyde) and various triamines in a 2:1 molar ratio those are known to afford a mixture of both the Schiff dibases and their cyclic analogues. Indeed, such ligands including several functions namely amine, imine, pyridine and imidazolidine (hexahydropyrimidine) are able to provide nitrogen donors allowing tuning of the ligand field around the metal center, and thereby, may lead to significant improvement of the catalytic activity. Furthermore, cobalt(II) complexes with nitrogen rich ligands are found to produce µ-peroxo bridged dinuclear complexes by the transfer of electrons from the metal centers to the oxygen molecule. I envisioned that condensation product of aromatic aldehyde (ketone) and various triamines may at least partly activate molecular dioxygen, thereby, capable to show various oxidase activity. Keeping all these in mind, herein, I report the syntheses and characterizations of two peroxo-bridged dicobalt(III) complexes, $[Co_2(L^1)_2(\mu-O_2)](ClO_4)_4 \cdot 2CH_3CN$ (1) and $[Co_2(L^2)_2(\mu-O_2)](ClO_4)_4$ (2), and three mononuclear cobalt(II) complexes, [Co(L³)(CH₃CN)](ClO₄)₂ (3), [Co(L⁴)(H₂O)](ClO₄)₂ (4) and $[Co(L^5)(H_2O)](ClO_4)_2$ (5), where L^1-L^5 are pentadentate ligands as shown in Scheme 1. The preferential complexation ability of all the ligands to the cobalt center irrespective of its oxidation state, and in one case (3) methanol addition across the -C=N- bond, are analyzed on the basis of the obtained structural data. The phenoxazinone synthase-like activity and its detailed kinetic investigations for all the complexes have also been described. This study not only provides ample information regarding the role of the metal ions and other factors on the relative stability of condensation products and the



Scheme 1 Drawing of the ligands characterized in the present study.

ability of selective dioxygen complexation but also shows the catalytic activity similar to the phenoxazinone synthase.

Experimental section

Materials and physical measurements

Chemicals such as 2-pyridinecarboxaldehyde, 6-methyl-2-pyridinecarboxaldehyde, 2-acetylpyridine, diethylenetriamine, 3,3'-diamino-*N*-methyldipropylamine, 3,3'-bisaminopropylamine, cobalt(II) perchlorate hexahydrate (Aldrich) and *o*-aminophenol (Merck, India) were of reagent grade, and used without further purification. Solvents like methanol, diethyl ether, and acetonitrile (Merck, India) were of reagent grade and used as received.

Microanalyses for C, H and N were carried out using a Perkin-Elmer 240 elemental analyzer. The infrared spectra of the complexes in KBr pellets were recorded in the 400-4000 cm⁻¹ range on a PerkinElmer Infrared spectrometer. Electrochemical data were collected on an EG&G Princeton Applied Research potentiostat model 263A with a Pt working electrode, Pt auxiliary electrode and Ag/AgCl reference electrode. Absorption spectra were measured using a UV-2450 spectrophotometer (Shimadzu) with a 1-cm-path-length quartz cell. Room temperature magnetic susceptibility measurements were performed in an EG and G PAR-155 vibrating sample magnetometer, using Hg[Co(SCN)₄] as a reference material; diamagnetic correction was made by Pascal's constants for all the constituent atoms. Electrospray ionization mass spectrometry (ESI-MS positive) was performed using a Micromass Q-tof-Micro Quadruple mass spectrophotometer.

Synthesis of the complexes

Caution! Perchlorate salts of metal complexes are potentially explosive and should be handled in small quantities and with great care.

 $[Co_2(L^1)_2(\mu - O_2)](ClO_4)_4 \cdot 2CH_3CN$ (1). Reaction of 3,3'-bisaminopropylamine (0.262 g, 2.0 mmol) with 2-pyridinecarboxaldehyde (0.428 g, 4.0 mmol) in a 30 ml of methanol under reflux for 45 min afforded a pale-yellow solution. Addition of Co- $(ClO_4)_2 \cdot 6H_2O$ (0.730 g, 2.0 mmol) dissolved in 20 ml of methanol to the resulting solution at room temperature instantly produced a light brown solution. The mixture was stirred in air for 30 min during which time a light brown powders separated out from the solution. It was collected by filtration and washed with mother liquor followed by methanol/ether and finally air dried. Yield: 1.020 g (82%). Single crystals suitable for X-ray diffraction were obtained from slow evaporation of acetonitrile solution of the complex after one week. Anal. Calcd for C40H52Cl4C02N12O18: C, 38.48; H, 4.19; N, 13.46. Found: C, 38.57; H, 4.09; N, 13.36. IR (KBr, cm⁻¹): 3235 w ($\nu_{\rm NH}$); 2854–3062 w (ν_{CH}); 1630 m ($\nu_{C=N}$); 1601 m ($\nu_{C=N, pv}$); 1145 s, 1114 s, 1087 s, 636 s, 626 s ($\nu_{\rm Cl-O}$); 777 w ($\nu_{\rm O-O}$). UV-vis $\lambda_{\rm max}$ / nm (ε /dm³ mol⁻¹ cm⁻¹) in methanol: 474 (3287), 438 (3264), 410 (3118), 322 sh (7220), 256 (20125). ESI-MS (positive) in methanol: Base peak was detected at m/z = 467.09 corresponding to $[Co(L^1)(ClO_4)]^+$.

 $[Co_2(L^2)_2(\mu-O_2)](ClO_4)_4$ (2). An identical synthesis as that of 1 was performed using 3,3'-bisaminopropylamine (0.262 g, 2.0 mmol), 2-acetylpyridine (0.488, 2.0 mmol) and Co- $(ClO_4)_2 \cdot 6H_2O$ (0.730 g, 2.0 mmol) as starting materials which led to 0.940 g, (77%) of a dark-brown crystalline materials. Crops of dark-brown crystals suitable for X-ray analysis were obtained from slow evaporation of acetonitrile solution of the complex at ambient temperature over one week. Anal. Calcd for C40H54Cl4Co2N10O18: C, 39.29; H, 4.45; N, 11.45. Found: C, 39.47; H, 4.39; N, 11.36. IR (KBr, cm⁻¹): 3248 br $(\nu_{\rm NH})$; 2856–30 862 w $(\nu_{\rm CH})$; 1639 m $(\nu_{\rm C=N})$; 1602 m $(\nu_{\rm C=N, py})$; 1145 s, 1117 s, 1087 s, 637 s, 626 s ($\nu_{\rm C-O}$); 780 m ($\nu_{\rm O-O}$). UV-vis $\lambda_{\text{max}}/\text{nm}$ (ϵ/dm^3 mol⁻¹ cm⁻¹) in methanol: 401 (4683), 272 (23 420). ESI-MS (positive) in methanol: A major peak was detected at m/z = 495.12 corresponding to $[Co(L^2)(ClO_4)]^+$.

[Co(L³)(CH₃CN)](ClO₄)₂ (3). A similar methodology as described for synthesis of 1 was carried out using 2-pyridinecarboxaldehyde (0.428 g, 4.0 mmol), diethylenetriamine (0.204 g, 2.0 mmol) and Co(ClO₄)₂·6H₂O (0.730 g, 2.0 mmol) as starting materials which yielded 0.730 g, (57%) of a red crystalline materials. Dark-red crystals suitable for X-ray diffraction were obtained from slow evaporation of acetonitrile solution of the complex after several days. Anal. Calcd C₂₁H₃₀Cl₂CON₆O₉: C, 39.39; H, 4.72; N, 13.12. Found: C, 39.37; H, 4.59; N, 12.94. IR (KBr, cm⁻¹): 3244 br (ν_{NH}); 2852–3076 w (ν_{CH}); 1632 m ($\nu_{C=N}$); 1599 m ($\nu_{C=N}$, _{py}) 1118 s, 1083 s, 622 s, 629 s (ν_{C-0}). UV-vis λ_{max}/nm (ε/dm^3 mol⁻¹ cm⁻¹) in methanol: 289 (20 878) 346 sh (1283). ESI-MS (positive) in methanol: base peak was detected at *m/z* = 499.10 corresponding to [Co(L³)(ClO₄)]⁺.

 $[Co(L^4)(H_2O)](ClO_4)_2$ (4). A mixture of 3,3'-bisaminopropylamine (0.262 g, 2.0 mmol) and 6-methyl-2-pyridinecarboxaldehyde (0.488 g, 4.0 mmol) was heated to reflux in a 30 ml of methanol for 45 min resulting in a yellow color solution and it was allowed to cool at room temperature. To the resulting yellow solution a 20 ml methanol solution of $Co(ClO_4)_2 \cdot 6H_2O$ (0.730 g, 2 mmol) was added and the mixture was stirred for 20 min. Orange crystalline materials containing single crystals for X-ray diffraction were separated out from the solution upon standing at room temperature overnight (1.128 g, 92% yield). Anal. Calcd for C₂₀H₂₉ Cl₂CoN₅O₉: C, 39.15; H, 4.73; N, 11.41. Found: C, 39.07; H, 4.89; N, 11.16. IR (KBr, cm⁻¹): 3428 br (ν_{OH}) ; 3220 br (ν_{NH}) ; 2854–3050 w (ν_{CH}) , 1654 m $(\nu_{\text{C=N}})$; 1600 m ($\nu_{C=N, pv}$); 1120 s, 1083 s, 625 s (ν_{Cl-O}). UV-vis λ_{max}/nm $(\varepsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1})$ in methanol: 276 (23 878), 332 sh (1481). ESI-MS (positive) in methanol: Base peak was detected at m/z =495.11 corresponding to $[Co(L^4)(ClO_4)]^+$.

[Co(L⁵)(H₂O)](ClO₄)₂ (5). An identical methodology as that described for 4 using 3,3'-diamino-*N*-methyldipropylamine (0.145 g, 1.0 mmol), 6-methyl-2-pyridinecarboxaldehyde (0.244 g, 2.0 mmol) and Co(ClO₄)₂·6H₂O (0.355 g, 1.0 mmol) yielded 0.502 g (88%) of crystalline materials including single crystals for X-ray quality of complex 5. Anal. Calcd for C₂₁H₃₁Cl₂CoN₅O₉: C, 40.16; H, 4.94; N, 11.16. Found: C, 40.07; H, 4.99; N, 11.06. IR (KBr, cm⁻¹): 3420 br ($\nu_{OH/NH}$); 2839–3062 w (ν_{CH}); 1654 m ($\nu_{C=N}$); 1600 m ($\nu_{C=N}$, py); 1107 s/br, 623 s (ν_{CI-O}). UV-vis λ_{max} /nm (ε/dm³ mol⁻¹ cm⁻¹) in methanol: 292 (19 870) 354 sh (1383). ESI-MS (positive) in methanol: Base peak was detected at m/z = 509.12 corresponding to [Co(L⁵)(ClO₄)]⁺.

X-ray crystallography

Single crystal X-ray diffraction data for complexes 1-5 were collected on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Several scans in φ and ω directions were made to increase the number of redundant reflections and were averaged during refinement cycles. Unit cell determination, data processing and structure solution were performed using the Bruker Apex-II suite program. All available reflections to $2\theta_{max}$ were harvested and corrected for Lorentz and polarization factors with Bruker SAINT plus.²⁶ Absorption corrections, inter-frame scaling, and other systematic errors were performed with SADABS.²⁶ All the structures were solved by the direct methods and all non-hydrogen atoms were refined anisotropically by full-matrix least squares based on F^2 using the SHELXL-97²⁷ program within the WINGX package²⁸ considering all available reflections. During the development of the structure it became apparent that few atoms in 2, namely C9 and O6-O12, were disordered. These disordered atoms were allowed to refine freely, and the final occupancy parameters were rounded up and fixed. While refining anisotropically, the U_{eq} values of O6-O8 were larger than usual and thus ADP restraints were applied in order to make them reasonable. The U_{eq} values of oxygen atoms of one perchlorate ion in other structures (except 5) were also reasonably larger than usual, but no elec-

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Compound	1	2	3	4	5
Empirical formula	C40H52Cl4C02N12O18	C40H54Cl4C02N10O18	C ₂₁ H ₃₀ Cl ₂ CoN ₆ O ₉	C ₂₀ H ₂₉ Cl ₂ CoN ₅ O ₉	C ₂₁ H ₃₁ Cl ₂ CoN ₅ O ₉
Formula weight	1248.60	1222.59	640.34	613.31	627.34
Temperature (K)	150(2)	150(2)	150(2)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	C2/c	$P2_1$	$P2_1/a$	$P2_1/n$
a(A)	10.5833(5)	20.0273(6)	9.324(4)	18.261(1)	8.3498(1)
$b(\dot{A})$	10.7937(5)	12.7577(5)	7.978(2)	8.2488(5)	20.2191(3)
c (Å)	12.7878(6)	21.1058(8)	18.741(8)	19.086(1)	15.6642(3)
α (°)	82.279(3)	90	90	90	90
βΘ	71.692(3)	110.357(2)	93.935(2)	117.836(3)	99.775(1)
γ(°)	64.544(3)	90	90	90	90
Volume (Å ³)	1252.20(10)	5055.8(3)	1390.8(9)	2542.3(2)	2606.12(7)
Z	1	4	2	4	4
$D_{\rm calc}$ (g cm ⁻³)	1.656	1.606	1.529	1.602	1.594
Absorption coefficient	0.962	0.950	0.868	0.945	0.923
(mm^{-1})					
$\widetilde{F}(000)$	642	2520	662	1268	1300
θ Range ion (°)	2.68-27.44	3.31-26.37	2.98-29.95	3.45-27.51	3.61-27.49
Reflections collected	9526	18 412	8951	8013	11 684
Independent	5644/0.0340	5119/0.0368	6274/0.0545	5136/0.0396	5959/0.0181
reflection/ R_{int}					
Data/restraints/	4361/0/326	3970/1/366	5430/1/340	3484/4/311	5003/0/354
parameters					
Goodness-of-fit on F^2	1.051	1.045	1.135	1.044	1.025
Final <i>R</i> indices	$R_1 = 0.0945$,	$R_1 = 0.0789$,	$R_1 = 0.1080$,	$R_1 = 0.0995$,	$R_1 = 0.0290,$
$[I > 2\sigma(I)]$	$wR_2 = 0.2130$	$wR_2 = 0.2089$	$wR_2 = 0.2657$	$wR_2 = 0.2549$	$wR_2 = 0.0695$
R indices (all data)	$R_1 = 0.1183,$	$R_1 = 0.1005,$	$R_1 = 0.1170,$	$R_1 = 0.1399,$	$R_1 = 0.0393$,
($wR_2 = 0.2426$	$wR_2 = 0.2272$	$wR_2 = 0.2755$	$wR_2 = 0.2840$	$wR_2 = 0.0742$
A mules (all data)	$wR_2 = 0.2426$	$wR_2 = 0.2272$	$wR_2 = 0.2755$	$wR_2 = 0.2840$	$wR_2 = 0.0742$

tron density around these atoms was found and therefore only ADP restraints were applied for these cases. Hydrogen atoms were mostly included in the structure factor calculation in geometrically idealized positions with thermal parameters depending on the parent atoms by using a riding model. Rests of them were located in the difference Fourier maps and were isotropically treated based on their respective parent atoms. Relevant crystallographic data together with refinement details for 1–5 are listed in Table 1.

Kinetics of the phenoxazinone synthase activity

The phenoxazinone synthase mimicking activity of all the five complexes was studied by the UV-vis spectroscopy in dioxygen saturated methanol using o-aminophenol (OAPH) as a substrate at 25 °C. Kinetics of the aerobic oxidation of OAPH catalyzed by 1-5 was investigated monitoring growth of the absorbance as a function of time at 435 nm ($\varepsilon = 24 \times 10^3 \text{ M}^{-1}$ cm⁻¹), which is characteristic of 2-aminophenoxazine-3-one in methanol. In order to determine the dependence of the rates on the substrate concentration and various kinetic parameters, 1×10^{-5} or 2×10^{-5} M solution of the complexes were treated with at least 10 equivalents of the substrate so as to maintain the pseudo-first-order condition. Similarly, varying amounts of the catalyst, $(5-600) \times 10^{-5}$ M, were treated with a fixed concentration $(1 \times 10^{-2} \text{ M})$ of the substrate in dioxygen saturated methanol in order to examine the catalyst dependency on rate of the reaction. The rate of a reaction was determined by linear regression from the slope of absorbance versus time plot and averaged over three independent measurements.

Results and discussion

Syntheses and general characterizations

Condensation of 2-acetylpyridine with triamine exclusively results Schiff dibasic ligand because methyl substitution on the azomethine-C not only reduces the electrophilic character of the imine-C but also increases the steric hindrance to the approaching nucleophile. On the other hand, it is well explored that the condensation of a triamine containing both primary and secondary amine groups with 2-pyridinecarboxaldehyde in 1:2 molar ratio yields a mixture of Schiff dibase and its heterocyclic analogue, and the ratio of which can be established by NMR spectroscopy.^{19,22} Recent reports disclosed that the metal-assisted ring opening/closing processes are common for such ligand systems, and several factors are responsible in this event including size of the metal ions, Lewis acidity, and stereochemistry of the metal centers.^{18-22,29} Keeping all these in mind, various triamines were allowed to react with 2-acetylpyridine or 2-pyridinecarboxaldehyde (6-methyl-2-pyridinecarboxaldehyde) in 1:2 molar ratio at reflux that resulted yellow-orange condensation products. Treatment of *in situ* prepared ligands with $Co(ClO_4)_2 \cdot 6H_2O$ in aerobic condition afforded two peroxo-bridged dicobalt(m) complexes of $[Co_2(L^1)_2(\mu - O_2)](ClO_4)_4 \cdot 2CH_3CN$ (1) and $[Co_2(L^2)_2 - O_2(L^2)_3]$ $(\mu$ -O₂)](ClO₄)₄ (2), while the rests are mononuclear cobalt(II) complexes, $[Co(L^3)(CH_3CN)](ClO_4)_2$ (3), $[Co(L^4)(H_2O)](ClO_4)_2$ (4) and $[Co(L^5)(H_2O)](ClO_4)_2$ (5). For complexes 1 and 2, the cobalt(II) ions are oxidized by the molecular oxygen which in turn reduced to the peroxide ion, O_2^{2-} , that bridges the cobalt(III)

centers. Purity of the complexes was established by elemental analyses; those are consistent with the structural composition as found from the single-crystal X-ray crystallography. All the complexes are soluble in common polar organic solvents (*e.g.*, acetonitrile, methanol and DMF) as well as in water reflecting their ionic character.

The IR spectra of complexes 1-4 display moderately strong peaks in the range 3220-3248 cm⁻¹ that indicates N-H stretching vibration, while it overlaps with the OH stretching frequency of the coordinated water molecules in 5. The later is eventually observed at 3420 cm⁻¹ as a broad signal that corroborate the facts of extended hydrogen boning present in the solid state of 5. Similar broadening of stretching frequency of coordinated water molecule is found at 3428 cm⁻¹ for complex 4. In the IR spectra of complexes 1-5, a strong and sharp band due to azomethine $\nu(C=N)$ appears in the range 1625-1654 cm⁻¹. In addition, a sharp peak in between 1597 and 1601 cm⁻¹ is observed for all the complexes, which might be assigned to pyridyl C=N stretching. The most important feature of IR spectra for 1 and 2 is the appearance of a medium intense band for peroxo O-O stretching at 776 and 788 cm⁻¹, respectively, which fall in the same range as that reported in structurally characterized end-on bridged dicobalt(m) complexes.^{30,31} Moreover, the IR spectra show strong intense absorption band over the range of 1083-1120 cm⁻¹ which is unambiguously assigned to the stretching frequencies of perchlorate ions. The splitting or broadening of ν (Cl–O) band may results from the involvement of hydrogen bonding of ClO₄⁻ ions in the crystal lattices. The bending mode of vibration for ClO_4^- ions is observed in the range 622–633 cm⁻¹ for all the complexes and they are also broad as expected.

The electronic spectrum of complex 1 displays two bands and a shoulder at 474, 256 and 322 nm, respectively. The broad band at 474 and shoulder at 322 nm are attributed to the peroxide $\pi^* \rightarrow \text{Co}^{\text{III}}$ LMCT band,^{32,33} while higher energy band might be due to LLCT transition. However, in the electronic spectrum of 2, only two bands observe at 401 and 272. The former is convincingly assigned to peroxide $\pi^* \rightarrow \text{Co}^{\text{III}}$ LMCT band, later one is due to LLCT transition. Both the peroxo-bridged complexes are highly stable in solution even they can sustain at very high temperature (Fig. S1 ESI†). Nature of the electronic spectra for mononuclear cobalt(II) complexes 3–5 are similar as those exhibit LLCT band at 289, 276 and 292 nm, respectively. In addition, a relatively weak broad shoulder for these three complexes is observed in the range 332–354 nm that signs about the LMCT transition.

Structural studies

The dimeric compounds $\text{Co}_2(\text{L}^1)_2(\mu-\text{O}_2)](\text{ClO}_4)_4\cdot 2\text{CH}_3\text{CN}$ (1) and $[\text{Co}_2(\text{L}^2)_2(\mu-\text{O}_2)](\text{ClO}_4)_4$ (2), crystallize in the centrosymmetric triclinic $P\bar{1}$ and monoclinic C2/c space groups, respectively, where the asymmetric unit in both the cases corresponds to half of the molecule. The perspective view of the complex cations of 1 and 2 are depicted in Fig. 1 and 2, respectively, together with the atomic numbering scheme. Important bond lengths are displayed in Table 2, while selected bond angles



Fig. 1 Molecular structure of 1 showing $C-H\cdots\pi$ stacking interactions. Ellipsoids are drown in 30% probability and most of the hydrogen atoms are omitted for clarity.



Fig. 2 Crystal structure of **2** showing $C-H\cdots\pi$ stacking interactions. Ellipsoids are drown in 30% probability and most of the hydrogen atoms are omitted for clarity.

Table 2 Selected bond lengths (Å) for complexes 1-5

	1	2	3	4	5
Co1-N1	1.949(5)	1.923(4)	2.233(6)	2.189(7)	2.2731(14)
Co1-N2	1.940(5)	1.951(5)	2.101(6)	2.074(7)	2.0926(14)
Co1-N3	1.994(5)	1.996(4)	2.161(6)	2.196(8)	2.2057(14)
Co1-N4	1.904(5)	1.930(4)	2.179(6)	2.067(7)	2.0848(14)
Co1-N5	1.997(5)	1.980(4)	2.182(6)	2.255(6)	2.2466(14)
Co1-O1/N6	1.864(4)	1.885(4)	2.168(6)	2.181(5)	2.1444(13)
O1-O1a	1.439(8)	1.439(7)	_	_	_ ``
Co1-Co1a	4.479(1)	4.529(1)	—	—	—

are found in Table S1 (ESI[†]). The complex cations in **1** and **2** are formed by a μ -peroxo-bridged Co^{III} dimer, and in the molecular structure, two metal centers are related to each other through an inversion center, which is located at the midpoint of peroxo bond that bridges two centrosymmetrically related metal centers in an end-on fashion. The peroxo nature of the dioxygen bridge is confirmed by the O–O distance of 1.439(8) Å in **1** and 1.439(7) Å in **2**, and separation of the metal centers are found to be 4.479(1) and 4.529(1) Å in **1** and **2**, respectively.

These metal-metal separations are significantly longer than those doubly bridging systems^{30,32} but comparable to the reported complexes in which only peroxo unit bridges two Co^{III} ions by means of an end-on (*trans*) fashion.^{34–36} The charge neutralization of the complexes is ensured by the presence of four perchlorate counter ions and each of them sits on a general position in **1**, while two perchlorate ions reside on a special position in the asymmetric unit of **2**, one being situated on a 2-fold axis and the remaining one in an inversion center.

The geometry of the metal centers in these complexes can be best described as pseudo-octahedral structure, comprised of five nitrogen atoms from pentadentate ligands $(L^1 \text{ or } L^2)$ and a bridging peroxide oxygen atom. The pyridyl rings are found to cis to each other and approximately perpendicular to each other (dihedral angle 81.30° for 1 and 75.45° for 2), but one of them is in trans to peroxo group which is different from the previously reported structure derived from the reduced Schiff base ligands of similar kinds.^{35,36} The Co-N bond distances fall in the range 1.904(5)-1.997(5) for 1 and 1.923(4)-1.996(5) for 2, while Co-O bond lengths are 1.864(4) and 1.885(4) for 1 and 2, respectively, consistent with the low-spin state of Co^{III} centers. The low-spin state of the metal ions in 1 and 2 is further supported by the fact of diamagnetic characteristics of these complexes at room temperature. Pyridyl-N bond length [1.997(5) for 1, 1.980(4) for 2] trans to the peroxo group is somewhat longer than cis disposed pyridyl-N [1.949(5) for 1, 1.923(4) for 2], which essentially arises from the stronger trans influence exerted by dioxygen moiety. The considerable distortion from the ideal octahedral geometry (90°/180°) is reflected from the transoid and cisoid angles as can be seen from Table S1 (ESI[†]). The crystal packing of the complexes is eventually stabilized by the strong electrostatic force of attraction between +4 charges of complex cations and perchlorate ions, and interestingly they form alternative layers in the crystal lattice (Fig. S2 and S3 ESI† for 1 and 2, respectively). In addition, hydrogen bonds involving lattice acetonitrile and secondary amine in 1, and in between secondary amine and the crystallographically ordered perchlorate ion in complex 2, are observed (Table 3). That solvate acetonitrile molecule

Table 3	Selective	hydrogen	bonds	in 1-	-5
Table J	Jelective	nyurogen	DOLID		

	D–H···A	D-H	Н…А	D····A	<d-h····a< th=""></d-h····a<>
1	N3-H3N…N6	0.93	2.29	3.205(8)	166
2	N3-H3N····O4 ^a	0.91	2.07	2.975(7)	173
3	N3-H3N····O2 ^c	0.93	2.40	3.170(16)	140
	N3-H3N····O5 ^c	0.93	2.31	3.187(11)	158
	N4-H4N····O3	0.93	2.46	3.265(16)	145
	N4-H4N····O4	0.93	2.46	3.323(17)	155
4	O1-H1A····O6 ^b	0.88	2.46	3.04(2)	124
	O1-H1A····O8 ^b	0.88	2.39	3.058(17)	133
5	O1-H1A…O5	0.84	2.02	2.834(2)	165
	O1-H1B…O8	0.78	2.05	2.817(2)	171

Symmetry code: a = 1/2 - x, -1/2 + y, 1/2 - z; b = -1/2 + x, 1/2 - y, z; c = -1 + x, y, z; d = 1/2 - x, 1/2 + y, 1/2 - z.



Fig. 3 Molecular structure of 5 showing atom numbering scheme. Ellipsoids are drawn in 30% probability level and hydrogen atoms are omitted from clarity.

further interacts with the pyridyl ring by means of a π - π staking interaction (not shown) in **1**.

The molecular structures of 3-5 are very similar and a representative structure of 5 is displayed in Fig. 3, while rests of them are shown in Fig. S4 and S5 (ESI⁺) for 3 and 4, respectively. Important bond lengths are displayed in Table 2, while selected bond angles are found in Table S1 (ESI[†]). Complexes 4 and 5 crystallize in the monoclinic centrosymmetric space groups $P2_1/a$ and $P2_1/n$, respectively, while complex 3 crystallizes in the monoclinic chiral space group P21 which might be due to the asymmetric nature of ligand L³ resulting in the chiral tunnels. All these three complex cations adopt a distorted-octahedral structure (see Table S1 ESI†) being exclusively coordinated by five donor sites of the pentadentate ligands in an identical manner as found in **1** and **2**,³⁷ and the coordination sphere is completed by either of water molecule (in 4 and 5) or acetonitrile molecule (in 3). The charge of the complex cation in all these cases is ensured by the presence of two perchlorate ions in the crystal structures. The structures of 4 and 5 are very similar but only difference is that the central amine hydrogen in 5 is being substituted by a methyl group. However, they are significantly different from 3 in that the central amine nitrogen is connected by two shorter ethylene linkers in 3 instead of propylene linkers for others (Scheme 1); in addition, one azomethine group in 3 is modified by the addition of methanol molecule across the -C=N- bond.19,38 The Co-N bond distances in all the three complexes are very similar and they vary in the range 2.101(6)-2.233(6) for 3, 2.067(7)-2.255(6) for 4 and 2.0848(14)-2.2731(14) for 5. The Co-O distance for coordinated water molecule is found to be 2.181(5) and 2.1444(13) for complexes 4 and 5, respectively. These bond lengths are along with the line of the reported high-spin cobalt(II) complexes having similar coordination environment.³⁹ The room temperature magnetic moment values [3.97, 4.08 and 4.12 BM for 3, 4 and 5, respectively] further support the high-spin state of the central cobalt(II) ions



Fig. 4 One dimensional (1D) hydrogen boded supramolecular chain of **3** propagating along the *a* axis.

in these complexes. The solid state packing of 5 as shown in Fig. S6 (ESI[†]) is stabilized by the hydrogen bonding interaction between perchlorate ion acceptor and coordinated water molecule and aromatic C–H donors. But molecular packing in 3 and 4 are very interesting; it forms 1D supramolecular straight chain resulting from the hydrogen bonding interaction between perchlorate ions and secondary amines in 3 (Table 3, Fig. 4), while wavy supramolecular chain propagating along the crystallographic *a* axis results from the hydrogen bonds involving secondary amine, coordinated water molecules and perchlorate ions, later being acted as a sole hydrogen acceptor in 4 (Table 3, Fig. S7 ESI[†]).

A number of information can be obtained from the X-ray crystal structures of the complexes. As shown in Fig. 1 and 2, the end-on peroxo-bridge is to some extent supported by C-H... π interaction in both the complexes. Although the O-O bond length in 1 and 2 is identical, but the Co-O-O angle is slightly smaller in 1 $[112.4(4)^{\circ}]$ than that found in 2 [113.0(4)°], and this difference in bond angles results the longer metal-metal separation in 2 [4.529(1) Å] than that of 1 [4.479(1) Å]. These observations suggest that methyl substitution at imine-C atoms in L² increases some sort of steric congestion around the metal center thereby preventing the closer approach of the metal centers to each other during the dioxygen complexation. The longer Co-O distance of 1.885(4) Å in 2 than that of 1.864(4) Å in 1 is also consistent with the above fact. Literature reports on similar complexes with reduced Schiff bases show that both the pyridyl groups are *cis* to each other even also cis to peroxo moiety and in those cases the central secondary amine is occupied trans to the dioxygen ligand.^{35,36} The authors pointed out that pyridyl group may compete with the dioxygen moiety in π -back donation if it occupies trans position of the peroxo unit, and thereby, the systems may not be stable enough. Indeed, this proposition was well supported by the fact that in all the structurally characterized peroxo-bridged complexes so far the trans position of the dioxygen moiety is occupied by a σ -donor atom,⁴⁰⁻⁴⁵ only exception is the recent report by Fukuzumi *et al.* where the *trans* position is occupied by a pyridyl group.⁴⁶ The present work is also further strengthening the fact that a potentially π-acceptor ligand like pyridine may also stabilize enough the peroxo bridging in its trans position.

It is quite interesting to note that although the ligands in the present study are very similar but L^1 and L^2 could only able to produce peroxo-bridged dicobalt(m) complexes, whereas in other cases they are mononuclear and oxidation state of the metal is also +2. The mechanism of formation of peroxobridged dinuclear complexes is well known in which both the metal centers donate one electron to molecular dioxygen and each of the metal ions is oxidized by one unit (Scheme S1 ESI[†]). This proposition suggests that the closer approach of two metal centers having unsaturated coordination number towards the molecular dioxygen along with the electron donating ability of metal centers play vital roles for such dioxygen binding ability. Effect of the methyl substitution at azomethine-C is already noticed in the crystal structure of 2 where increased steric congestion enforces the metal centers to stay away from each other. Similar to ligand L^2 , ligands L^3 and L^4 have also two methyl substitutions but the position of substitution is different and that is probably the reason for such chemical diversity. Careful inspection of bond distances reveals that secondary amine bond distances are longer than the pyridyl moieties in 1 and 2 (see Table 2), which is consistent with the state of hybridization of nitrogen atoms. But reverse trend is observed in complexes 3-5, which suggests that the methyl substitution in pyridine ring at the sixth position offering significant steric congestion, and thereby, leads to a weaker coordination ability of pyridyl-N atoms in these complexes.^{47,48} Based on the above observations one can conclude that both the steric and electronic factors are involved in the dioxygen binding ability of the complexes. Firstly, the reduced donation from pyridyl nitrogen to cobalt decreases significantly drifting of electron towards the molecular dioxygen. Secondly, the steric congestion offered by the methyl substituents diminishes the possibility of closer approach to each other which is similar to the biological system where steric hindrance of globin chains in hemoglobin inhibits the peroxo bridging thereby preventing the formation of hematin.

It is now well explored that aromatic aldehyde reacts with triamine having central secondary amine functionality produces both Schiff dibase and its heterocyclic analogue,19,22 and substitution like methyl group at pyridine should not have much impact on such isomerization. Thus in situ prepared Schiff base ligands of L¹, L³ and L⁴ are expected to stay in equilibrium with their heterocyclic analogues. But isolated products suggest that they are in Schiff dibasic form in all the complexes although one arm of the Schiff base is modified by the addition of methanol across the azomethine moiety in 3. The yields of these reactions also unambiguously tell the story of the ring opening of such condensed heterocyclic forms during complexation. As mentioned earlier, mainly two factors (Lewis acidity and size of the metal ion)^{19,20} are well explored on the selective binding ability of the ligands and/or ring opening and closing phenomena. The binding of L^1 in complex 1 agrees well with both of these factors as the central cobalt(III) has smaller ionic radius and also high Lewis acidity. But the complexation of L^3 and L^4 in 3 and 4, respectively, does not support either of the factors. The remark of Tuchagues et al.¹⁹ about the prominent role of the ionic radius over the Lewis acidity (postulation of Boča et al.) also breaks down in the present finding as the ionic radius of Co^{II} (83.5 pm) is

even larger than that of Ni^{II} (83 pm).⁴⁹ It is worth noting that Mn, Fe, Ni, Cu and Zn complexes have been structurally characterized in both the isomeric forms of the ligands,^{18–20} but the present results establish that it is the Co that exclusively prefers the Schiff-dibasic form of the ligands even irrespective of its oxidation state.

Electrochemical studies

Since the function of a redox active metalloenzyme is to catalyze a redox process, thus electrochemical properties are important factors in determining the catalytic activity of their model complexes although significant modification of potentials may occurs in a chemical reaction especially if the reactants interact with each other. The electrochemical data of the complexes have been recorded in methanol containing 0.1 M tetraethylammonium perchlorate as a supporting electrolyte at a platinum working electrode and using a Ag/AgCl reference electrode. The cyclic voltammogram of 3 is shown in Fig. 5 and while for 2 in Fig. S8 (ESI⁺), and the electrochemical data for all the complexes are given in Table 4. Electrochemical behavior of both peroxo-bridged complexes 1 and 2 are similar in that they are irreversibly reduced to cobalt(m) from cobalt(m) at the electrode surface. The irreversible nature may be due to the significant modification of reduced species in term of loss of bridging peroxide as similar behavior is also observed at inert condition. In contrast, the electrochemical responses of 3-5 are quasi-reversible and these electrochemical responses are due the cobalt(III)/cobalt(II) couple. The electrochemical properties of these complexes are very similar to the reported results of related complexes.50

Phenoxazinone synthase like activity

The phenoxazinone synthase mimicking activity of the complexes was studied by monitoring the oxidation of *o*-amino-



Fig. 5 Cyclic voltammogram of 4 in methanol containing tetraethylammonium perchlorate as the supporting electrolyte at a scan rate of 100 mV s⁻¹.

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 Table 4
 Electrochemical data for 1–5 in methanol^a

Complex	$E_{\rm p}^{\rm c}$ (V)	$E_{\mathrm{p}}^{\mathrm{a}}\left(\mathrm{V} ight)$	$\Delta E_{\rm p}$ (V)
1	-0.583	_	_
2	-0.626	_	_
3	-0.382	-0.084	-0.298
4	-0.437	-0.075	-0.372
5	-0.453	-0.082	-0.371

 a Pt working and Ag/AgCl reference electrodes; supporting electrolyte tetraethylammonium perchlorate; scan rate 100 mV s⁻¹.



Fig. 6 Time resolved UV-vis spectral changes for the oxidation of *o*-aminophenol (1.0×10^{-2} mol dm⁻³) catalyzed by **1** (1×10^{-5} mol dm⁻³) for up to 2 h of reaction in dioxygen-saturated methanol at 25 °C.

phenol (OAPH) spectrophotometrically in dioxygen-saturated methanol at 25 °C. In order to avoid the autoxidation of the substrate by air the catalytic activity was examined in the absence of an added base. Prior going to the detailed kinetic study, it is important to check the ability of the complexes to behave as catalyst for the oxidation of o-aminophenol, and for this purpose 1.0×10^{-5} or 2.0×10^{-5} M solutions of the complexes were treated with a 0.01 M solution of o-aminophenol, and the spectra were recorded in dioxygen saturated methanol at 25 °C. The time dependent representative spectral changes for a period of 2 h after the addition of OAPH are shown in Fig. 6 and 7, for 1 and 4, respectively. The spectral scans reveal the progressive increase of peak intensity at ca. 435 nm, characteristic of phenoxazinone chromophore, suggesting catalytic oxidation of OAPH in aerobic condition. It may be noted here that a blank experiment without catalyst does not show significant growth of the band at 435 nm in an identical reaction condition. These spectral behaviors conclude that all the complexes show phenoxazinone synthase like activity in aerobic condition.



Fig. 7 UV-vis spectral scan for the oxidation of o-aminophenol (1.0 × 10^{-2} mol dm⁻³) catalyzed by 4 (2 × 10^{-5} mol dm⁻³) for up to 2 h of reaction in dioxygen-saturated methanol at 25 °C.

Kinetic studies were performed to understand the extent of the catalytic efficiency. For this purpose, a 1×10^{-5} M solution of 1 and 2 or 2×10^{-5} M solution of 3-5, were treated with at least 10-fold concentrated substrate solution so as to maintain the pseudo-first-order condition. All the kinetic experiments were carried out at a constant temperature of 25 °C, monitored with a thermostat under aerobic conditions. For a particular complex-substrate mixture, time scan at the maximum band of 2-aminophenoxazine-3-one was performed for a period of 30 min. The initial rate of the reactions versus concentration of the substrate data show a rate saturation kinetics as can be seen from Fig. 8. This observation indicates that 2-aminophenoxazine-3-one formation proceeds through a relatively stable intermediate, a complex-substrate adduct, followed by the redox decomposition of the intermediate at the rate determining step. This type of saturation rate dependency can easily recall the Michaelis-Menten model, originally developed for the enzymatic kinetics, which on linearization gives double reciprocal Lineweaver-Burk plot to analyze values of various parameters like V_{max} , K_{M} , and K_{cat} . The representative observed and simulated initial rates versus substrate concentration of non-linear plot and the Lineweaver-Burk plot for complexes 1, 2 and 4 are shown in Fig. 8 and 9, respectively. Analysis of the experimental data yielded Michaelis binding constant (KM) and V_{max} , and the turnover number (k_{cat}) value is obtained by dividing the V_{max} by the concentration of the complex used, and these parameters are listed in Table 5. Moreover, for a particular substrate concentration, varying the complex concentration, a linear relationship for the initial rates is obtained, which shows a first-order dependence on the complex concentration (Fig. S9 ESI[†]).

As can be seen from Table 5, the turnover number (k_{cat}) for the oxidation of OAPH follows the order $1 > 2 \gg 5 > 4 > 3$. The



Fig. 8 Nonlinear plot of initial rates *versus* substrate concentration for the oxidation of *o*-aminophenol catalyzed by complexes **1**, **2** and **4**. Symbols and solid lines represent experimental and simulated profiles, respectively.



Fig. 9 Linear Lineweaver–Burk plot for complexes 1, 2 and 4. Symbols and solid lines represent experimental and simulated profiles, respectively.

Table 5 Kinetic parameters for phenoxazinone synthase activity of 1-5

Complex	$V_{\rm max}({\rm mol}\;{\rm dm}^{-3}\;{\rm s}^{-1})$	$K_{\rm M} ({ m mol} { m dm}^{-3})$	$K_{\text{cat}}\left(h^{-1}\right)$
1 2 3 4 5	$\begin{array}{l} 8.60 \ (\pm 0.09) \times 10^{-8} \\ 6.40 \ (\pm 0.08) \times 10^{-8} \\ 1.87 \ (\pm 0.06) \times 10^{-8} \\ 3.54 \ (\pm 0.06) \times 10^{-8} \\ 4.60 \ (\pm 0.08) \times 10^{-8} \end{array}$	$\begin{array}{l} 1.01 \left(\pm 0.15\right) \times 10^{-2} \\ 1.47 \left(\pm 0.16\right) \times 10^{-2} \\ 1.01 \left(\pm 0.14\right) \times 10^{-2} \\ 1.28 \left(\pm 0.15\right) \times 10^{-2} \\ 1.32 \left(\pm 0.17\right) \times 10^{-2} \end{array}$	30.09 23.04 3.36 6.37 8.28

higher reactivity of complexes 1 and 2 is most probably due to ease of the regeneration of the catalyst by molecular oxygen. Moreover, the high reactivity of 1 in comparison to 2 probably due to the steric hindrance of the two methyl substitution at azomethine-C towards the incoming substrate as well as during the regeneration of catalyst by the reaction of molecular dioxygen. Effect of the methyl substitution has already been noticed in the crystal structure of 2 where the metal---metal separation as well as Co-O bond distances is slightly longer than that found in 1. Although electrochemical behaviors of all the complexes are very similar but the lower reactivity of 3-5 can be explained by the chemical sense where the methyl substitution at sixth position of pyridine moieties decreases significantly the possibility of oxidation by molecular dioxygen chemically. The lowest k_{cat} value of 3 possibly due to the structural rigidity of the ligand although significant flexibility is gained by the addition of methanol molecule across one of the -C=N- linker. Moreover, the slightly higher reactivity of compound 5 in comparison to 4 can only be possible if the electronic features dominate over the steric factor that gained in the presence of an additional methyl group attached to central amine nitrogen in 5. Although not conclusive, the solid state structure of complex 5 is quite informative as it shows the methyl substitution under consideration occupying at the opposition site of the approaching substrate molecule. It is also worth noting that the present compounds especially 1 and 2 show even higher reactivity than our recently reported bis(imido)-bridged dicobalt(III) complex.²⁴ Such higher reactivity may be due to ease of molecular dioxygen activation in the present cases.

Conclusions

The present study demonstrates the syntheses and structural characterizations of two peroxo-bridged cobalt(III) complexes (1 and 2) and three mononuclear cobalt(II) complexes (3-5) derived from the condensation products of triamine and 2-acetylpyridine or 2-pyridinecarboxaldehyde (6-methyl-2-pyridinecarboxaldehyde). Literature survey reveals that Mn, Fe, Ni, Cu and Zn stabilize either of the isomeric forms (Schiff dibasic and heterocyclic) of the ligands,18-20 but from the present structural study it is clear that all the ligands exclusively bind the metal centers through Schiff dibasic form independent on the oxidation state of cobalt. Furthermore, the effect of methyl substitution (even also the position of substitution) on their crystal structures is noticed. Methyl substitution on azomethine-C does not inhibit the peroxo-bridging although increased steric congestion around the metal center prevents the close approach of metal centers to each other during the dioxygen activation as evidenced from the longer metal-metal separation found in 2 than that of 1. But the discrete effect has been observed (for 3-5) when substitution is present at sixth position of the pyridine ring, and in these cases both the steric and electronic factors prevent the formation of peroxo-bridging. All the complexes show phenoxazinone synthase mimicking activity and the relative extent of the catalytic activity has been examined. Although electrochemical behaviors of all the complexes are very similar, their relative catalytic activity mimicking the function of phenoxazinone synthase arises from the electronic and steric factors of the methyl substitution specifically at the position of the substitution.

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