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Single-Step Benzene Hydroxylation by Cobalt(II) Catalysts via Cobalt(III)-Hydroperoxo Intermediate

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The cobalt(II) complexes of tetradentate ligands (4N) have been synthesized and characterized as the catalysts for phenol synthesis in single-step. The molecular structure of complexes showed geometry in between square pyramidal and trigonal bipyramidal (τ , 0.49 – 0.88) with Co-N_{amine} (2.104 – 2.254 Å) and Co-N_{Py} bond distances (2.043 – 2.099 Å). The complexes exhibited Co²⁺/Co³⁺ redox potential around 0.489 - 0.500 V vs Ag/Ag⁺ in acetonitrile. The complexes catalyzed hydroxylation of benzene using H₂O₂ (30%) and afforded phenol selectively as a major product. The maximum yield of phenol up to 29% and turnover number (TON) of 286 at 60 °C and yield of 19% and TON of 191 at 25 °C are achieved. This is the highest catalytic performance reported using cobalt(II) complexes as catalysts to date. This aromatic hydroxylation presumably proceeded via cobalt(III)-hydroperoxo species, which was characterized by ESI-MS, vibrational and electronic spectral methods. The formation of key intermediate [(L)Co^{III}(OOH)]²⁺ was accompanied by the appearance of the characteristics O \rightarrow Co(III) ligand to metal charge transfer (LMCT) transition around 488-686 nm and vibration modes at 832 cm⁻¹ (O-OH) and 564 cm⁻¹ (Co-O). The geometry of one of the catalytically active intermediates was optimized by DFT and its spectral properties were calculated by TD-DFT calculations. These data are comparable to the experimental observations. The kinetic isotope effect (KIE) values (0.98 - 1.07) support the involvement of cobalt-bound oxygen species as a key intermediate. The isotope-labeling experiments using H₂¹⁸O₂ showed an 89% incorporation of ¹⁸O, reveals that H₂O₂ is the main oxygen supplier for phenol formation from benzene. The catalytic efficiencies of cobalt complexes are tuned by ligand architecture via their geometrical configurations and steric properties.

Introduction

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Phenol is an important raw material and chemical intermediate for the production of drugs, resins, dyes, caprolactam and etc.¹ Currently, phenol is produced in the industry via a three-step cumene process.² However, the process has disadvantages such as high energy consumption, poor yield of phenol and an equal amount of by-product acetone formation. To overcome these limitations, several researchers are focusing attention to design the catalyst that affords phenol selectively in a single-step without or with a minor amount of by-products. In fact, one of the main challenges in benzene hydroxylation is the activation of C-H bond (bond energy = 460 kJ mol⁻¹), often transition metal catalysts were employed.³ However, only limited progress has been made using transition metal complexes (V, Fe, Ni, Cu, Os, etc.)^{4a-g} and photocatalysts,^{4h} where eco-friendly oxidants such

as O₂, N₂O, and H₂O₂ were employed. The transition metalcontaining heterogeneous catalysts such as TS-1,^{5a} SBA-15,^{5b} and molecular sieves^{5c-d} were reported as less efficient catalysts due to leaching. Hence, the search for new catalysts for the production of phenol in a single-step is evergreen interest. In this context, the Co(III)-peroxo species are known to play a crucial role as active intermediates in electrophilic and nucleophilic reactions,^{6a,b} nonetheless, which are less exploited as catalysts for aromatic C-H activation/hydroxylation.^{6a} In 2016, Silva and co-workers have firstly reported cobalt(II)-N₂O₂ type of complexes as a catalyst for benzene hydroxylation with low catalytic efficiency.^{6c} In 2017, Fukuzumi and co-workers have reported photocatalytic hydroxylation of benzene using $[Co^{III}(Cp^*)(bpy)(H_2O)]^{2+}$ (Cp*= η^5 -pentamethylcyclopentadienyl and bpy = 2, 2-bipyridine) and photocatalyst $[Ru^{II}(Me_2Phen)_3]^{2+}$ in presences of O2, where TON of 500 and benzoquinone as a by-product were observed.4g In this article, we report the synthesis and characterization of cobalt(II) complexes of tetradentate ligands (Scheme 1) as the efficient catalysts for selective hydroxylation of benzene using H_2O_2 as an oxygen supplier. The ligand architecture, steric and electronic nature of ligands provide a significant difference from the previously reported catalysts and thus better catalytic performances. It is noteworthy that 29% of phenol formation is achieved by direct hydroxylation of benzene, which showed TON of 286 and turnover frequency (TOF) up to 57 h⁻¹. This is the highest yield

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and catalytic efficiency reported so far in the literature using cobalt(II) complexes as catalysts for hydroxylation of benzene. This conversion likely proceeds via Co(III)-peroxo species, which was studied by spectral and DFT methods.

Results and discussion

Synthesis and Characterization. The ligands L1 - L5 have been synthesized by the previously reported procedures.⁷ The cobalt(II) complexes [Co(L)Cl]X, **1** - **5** (X = ClO_4/BPh_4) were synthesized by the reaction of respective ligands and $CoCl_2 \cdot 6H_2O$, followed by the addition of an equivalent of NaClO₄/NaBPh₄ in methanol.⁸ All the complexes were characterized by HR-ESI, electronic spectra, redox methods, and their molecular structures were determined by single-crystal Xray crystallography studies. Four nitrogen atoms of ligand and a chloride ion constitute the [Co^{II}(4N)Cl]⁺ coordination sphere and a ClO₄/BPh₄ occupied at the outer coordination sphere (Figure 1). The complexes exhibited geometry in between square pyramidal and trigonal bipyramidal as predicted by Addison structural parameter, $\tau = 0.49 - 0.88.^9$ The complexes displayed almost identical Co-N_{amine} bond distances (2.104 - 2.254 Å) and are longer than Co-N_{Py} bonds (2.043 - 2.099 Å) due to relatively stronger overlapping of p-orbital of pyridine nitrogens with dorbital of Co^{II}-center. The Co-Cl bond distances are in the range of 2.2659 - 2.2817 Å (Table S1 - S2), apparently, they are labile and possibly replaced by solvent molecule followed by H₂O₂ during the catalysis (cf. below).



Scheme 1. The 4N-ligands used in the present study



Figure 1. The molecular structures of 1 (a), 2 (b), 4 (c) and 5 (d). The hydrogen atoms and counter ions are omitted for clarity.

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All the cobalt(II) complexes exhibited two absorption bands in the range of 472 - 528 nm (${}^{4}A_{2}$ to ${}^{4}E(P)$) and 59739628 nm (${}^{6}A_{2}$ to ${}^{4}E$) in acetonitrile.⁸ Also, the ligand-based π - π * transitions appeared around 271 - 284 nm.¹⁰ Interestingly, a very similar absorption bands were observed in solid-state (Figure S5), which clearly reveals that all the complexes retain their geometry in solution as well. The complexes showed a welldefined Co²⁺/Co³⁺ redox couple around 0.489 - 0.500 V vs. Ag/Ag⁺ in acetonitrile and are far away from the reversibility (Figure S11-S12). The Co²⁺/Co³⁺ redox potential of **1** - **3** (0.492 -0.500 V) and **4** - **5** (0.489 - 0.496 V) are almost identical.

Catalytic benzene hydroxylation. Catalytic hydroxylation of benzene investigated using Co(II)-complexes as catalysts and H_2O_2 (30%) as an oxygen source. The catalytic reaction was optimized using benzene (5 mmol), a catalytic amount of complex (5 µmol, 0.1 mol%) in acetonitrile (5.0 mL). Finally, H_2O_2 (25 mmol) was very slowly added into the reaction mixture under constant stirring at 60 °C and then the reaction was continued for 5 hours (Scheme 2). Afterward, the reaction mixture was passed through the silica column to remove the catalyst. The reaction mixture was analysed and quantified by GC-MS/GC (Figure S14).



Scheme 2. Catalytic benzene hydroxylation by Co(II) Complexes.

Table 1. (Catalytic	henzene h	vdrox	/lation	using	1 – 5
Table I.	Satarytic	DCHZCHC H	yurung	ration	using	

		,		,	,	0		
cat ^a	Tb	[C] ^c	[Y] ^d	[S] ^e	TON ^f	TOF ^g	KIE ^h	v
	(°C)	(%)	(%)	(%)		(h⁻¹)		(cm⁻¹) ⁱ
1	60	28	24	86	237	47	0.99	844.93
	25	16	14	87	142	28		
2	60	29	27	93	268	55	1.03	844.97
	25	18	17	94	171	34		
3	60	30	29	97	286	57	1.07	844.29
	25	20	19	95	191	38		
4	60	24	18	74	181	36	0.98	843.13
	25	16	13	81	134	27		
5	60	26	20	77	198	40	0.98	844.99
	25	16	14	87	162	32		

^aReaction condition: Benzene (5 mmol), complex (5 μ mol, 0.1 mol%) and hydrogen peroxide (30%) (25 mmol) in 5 mL acetonitrile at 25 °C/60 °C for 5 hours. ^b Temperature. ^c Conversion. ^d Yield. ^e selectivity. ^f Turnover number. ^g Turnover frequency. ^hCatalyst (5 μ mol), 1:1 mixture of C₆D₆ (2.5 mmol) and C₆H₆ (2.5 mmol), hydrogen peroxide (30%) (2.5 mmol) at 60 °C for 5 hours. ⁱ Solid-state IR data of **1a-5a**.

Complex **1** showed a lower yield of phenol (24%) and selectivity than **2** (27%). Interestingly, introducing electron releasing groups on pyridine arms of **2** to obtain **3**, resulted in **a** slight acceleration of phenol yield (29%) and much-improved selectivity (97%) than **1** and **2**. In fact, **1** - **3** are containing almost similar structural skeleton but they varied by electronic and steric substituents. The higher catalytic efficiency of **3** is possibly facilitated by the electron releasing groups on the ligand L3. On the other hand, the complex **4** containing sterically constrained diazepane backbone showed a lower yield of phenol, 18%, and selectivity (74%) than those of **1** - **3** (Table 1). While using **5** as catalyst showed a slight increase in phenol yield (20%) and

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selectivity (77%) than 4 (Figure S15, S16A). Generally, the complexes containing the tripodal backbone showed the highest catalytic efficiency than the sterically constrained cyclic diazepane backbone. The catalytic efficiency is strongly influenced by electronic and steric factors and decreasing order of catalytic efficiency is found as **3** > **2** > **1** > **5** > **4**. The calculated steric maps by SambVca 2.1A showed %V_{bur} of 70.7 - 71.6% for 1 - 3 are lower than that of 5 (74.6%) (Figure S18). The phenol formation exhibited by 3 is the maximum catalytic efficiency achieved so far in the literature using cobalt(II) complexes as the catalyst. In fact, it is a concomitantly higher yield than the previous reported Co(II) complex by Silva and co-workers, where 23% of phenol was reported using relatively higher catalyst loading (1 mol%).6c The copper^{12a} and iron complexes^{12b} were reported to catalyse lower yield of phenol, 14.6% and 19.9% respectively. However, the nickel complexes reported by us afforded 41% phenol yield, which is the highest yield known in the literature.13

The catalytic reactions were performed at 25 °C without altering other conditions specified in table 1. The complex 1 showed 14% of phenol formation with the selectivity of 87%. As expected, the complex 2 afforded a slightly enhanced yield of phenol (17%) and selectivity (94%). The yield of phenol further increased to 19% with the selectivity of 95% while using 3 as a catalyst. Similarly, the catalytic reaction performed using 4, showed 13% of phenol formation with the selectivity of 81%, which is lower than those of 1 - 3. The catalyst 5 showed slightly enhanced phenol yield (14%) and selectivity (87%) than 4 (Table 1, Figure S15, S16B), but it is still lower yield than those of 1 - 3. The catalytic efficiency trend is almost identical to that of observed at 60 °C, but their corresponding phenol yields are relatively lower. The influence of H₂O₂ loading was examined using the most efficient catalyst 3 at 60 °C and keeping other reaction conditions identical. Wherein, the yield of phenol was linearly increased on increasing the amount of H₂O₂ used, however, the selectivity was reciprocally declined (Figure S19, Table S5). Thus, the catalytic efficiency is strongly influenced by the amount of H_2O_2 used. Whereas, the reaction of equal amounts of benzene (5 mmol) and H_2O_2 (5 mmol) showed relatively lower yield, 17%, and TON, 172 at 60 °C for 1, which is further lowered to 9%, with TON of 91 at 25 °C under identical condition (Figure S17). Similarly, complexes 2 - 5 showed the relatively lower amount of phenol conversion under this condition, such as 2, 18%; 3, 20%; 4, 12% and 5, 13% at 60 °C and 2, 11%; 3, 14%; 4, 10% and 5, 12% at 25 °C (Table S6, Figure S17). Nevertheless, the selectivity is improved for all the catalysts as compared 5 equivalents of H₂O₂. In contrast, the higher yields of phenol are achieved for 5 equivalents of H₂O₂ (Figure S19). Interestingly, the bulk-scale reaction of benzene (30 mmol), catalyst 3 (50 μ mol) and H₂O₂ (50 mmol) showed the exclusive formation of phenol up to 0.27 g at 60 °C over 120 hours. Use of $CoCl_2 \cdot 6H_2O$ as catalyst did not show benzene hydroxylation under our experimental conditions.

While using phenol as a substrate and **3** as catalyst displayed no hydroxylated product formation under identical condition, and merely substrate was recovered quantitatively. In addition, toluene, anisole, chlorobenzene, and nitrobenzene were also

employed as substrates using catalyst 3 and five equivalents of H₂O₂ at 60°C over 24 hours. The tolueneo afforded combined yield of 17% (selectivity: o-, p-cresol, and benzaldehyde as 33%, 34%, and 33%) and without the formation of any guinone derivatives (Scheme 3, Figure S20). This is enlightening that the catalysts are capable of executing selective hydroxylation at aromatic sp² carbon.^{4e} Anisole showed the formation of o-, mand *p*-methoxyphenol as products with a combined yield of 22% (selectivity: 70%, 26%, 4% for o-, m-, p-substitutions respectively) (Figure S21). Whereas, chlorobenzene afforded oand *p*-chlorophenol as the products with the combined yield of 15% (Figure S22). The nitrobenzene poorly converted into oand p-nitrophenol (8%) (Figure S23). Reactivity of substituted benzene is correlated with Hammett constants (Figure S24), which shows electron-donating groups such as -Me and -OMe showed better hydroxylation than the electron-withdrawing group.^{3b, 4f} However, all these yields are relatively lower than those exhibited by benzene (Table S7), which clearly suggests that the catalyst 3 is efficient and selective towards monohydroxylation of benzene.



Scheme 3. Catalytic hydroxylation of toluene by 3.

Mechanism of benzene hydroxylation. The kinetic isotopic effects (KIE) were determined by employing 1:1 ratio of C_6H_6 (2.5 mmol) and C_6D_6 (2.5 mmol) as substrates at 60 °C over 5 hours. The KIE values were calculated as 0.98 - 1.07 for 1 - 5 from the ratio of products C₆H₅OH and C₆D₅OH using GC-MS/GC data (Figure S25, S26 and Table 1). Very similar KIE values (0.9 -1.0) were reported for intramolecular aromatic hydroxylation. In fact, the KIE value ~1.0 is reported for aromatic hydroxylation using metal-bound oxygen species as key intermediate via electrophilic aromatic substitution reaction.¹⁴ The results show that benzene C-H bond cleavage is not involving in the ratelimiting step. Also, KIE values suggest that benzene hydroxylation is not proceeded via a radical type reaction, whereas the KIE value of Fenton's type reaction is reported in the range of 1.7 – 1.8.^{15a} The KIE values were determined over various time intervals and showed values of ~1.0 throughout the reaction time (Figure S27). Catalysis using TEMPO as a radical trapping agent and catalyst 3, showed almost no changes in the phenol yield and ruled out the possibility of involvement of radical type mechanism. Further, benzene hydroxylation was carried out using mixed CH₃CN: CCl₄ (4:1) solvents, showed selectivity of 95% for phenol formation and 5% of chlorobenzene as a minor product at 60 °C (Figure S28). This revealing that the use of a radical trapping agent (CCl₄) did not significantly affect the selectivity of phenol and supports further to exclude the radical type reaction pathway.^{4f} The oxidation of cis-1,2-dimethyl cyclohexane under similar reaction conditions using 3 as catalyst exhibited 2% of cis hydroxylated product formation with the trace of trans product. In another experiment, cyclohexane was used as a substrate

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and CCl₄ as a radical trapping agent, which showed a combined yield of 3% (selectivity = 93% and 7% of cyclohexanol and cyclohexanone respectively) and without the formation of cyclohexyl chloride (Figure S29). All these observations strongly support to exclude the possibility of radical type reaction in benzene hydroxylation. Further, the metal insertion reaction type may not be involved in the mechanism, which is known to display KIE values of 2.0 – 4.8.^{15b} Isotope labelling studies were performed to authenticate the origin of oxygen atom, where we employed the most active catalyst **3** and $H_2^{18}O_2$ with 90% atom purity in H₂O at 60 °C. The result showed nearly 89% of ¹⁸O incorporation into the product as ¹⁸O labelled phenol determined by GC-MS (Figure S30). Under the identical reaction conditions, the reaction was carried out using $H_2^{18}O$ and H_2O_2 , where no ¹⁸O atom incorporation was determined by GC-MS. This is clearly revealing that the H₂O₂ is the key oxygen supplier for the formation of phenol from benzene.^{15c}

The aromatic hydroxylation reaction likely proceeds via species, cobalt(III)-peroxo which were characterized spectroscopically and possible geometries were optimized by DFT calculations. The cobalt(III)-peroxo species of 1 - 5 were generated by adding 10 equivalents of H₂O₂ and 2 equivalents of Et_3N in acetonitrile at -40 °C, which exhibited the formation of thermally stable species. In particular, the treatment of 10 equivalents of H_2O_2 (30%) to 3 and 2 equivalents of Et_3N exhibited a color change from purple to yellow at -40 °C in acetonitrile. Where the new absorption bands were appeared at 385 nm (ϵ , 2280 M⁻¹ cm⁻¹; k_{obs} , 1.7 ± 0.0003 × 10⁻² s⁻¹, $t_{1/2}$, 40 s), 553 nm (*ε*, 315 M⁻¹ cm⁻¹) and 576 nm (*ε*, 275 M⁻¹ cm⁻¹) (Figure S31). The HR-ESI mass spectrum showed a prominent peak at m/z, 491.0321 corresponds to $[Co^{III}(L3)(O_2)]^+$ 3a (calculated m/z, 491.2068). Further, the same species was generated using isotopically labelled H₂¹⁸O₂ (90% ¹⁸O atom), which resulted in a prominent shift in m/z value, 495.2139 and is ascribed to [Co^{III}(L3)(¹⁸O₂)]⁺ (Figure S32). The four-mass unit shift upon the substitution of ¹⁶O₂ with ¹⁸O₂ indicates that the intermediate species has two oxygen atoms. In solid, the FT-IR spectrum showed the vibrational band at 840 cm⁻¹ corresponds to O-O stretching frequency (Table 1). $^{\rm 16}$ The intermediate showed a well-shifted oxidation potential (E_{pa} , 0.640 V) from **3** and suggests that there is a change in the oxidation state of cobalt (Figure S33). Similarly, the key intermediate $[Co^{III}(L)(O_2)]^+$ of other complexes 1a, 2a, 4a, and 5a were generated under identical conditions. They showed similar electronic spectral changes and kinetics (Figure S34 - S36; Table S8). Further, their formations were confirmed by ESI-MS spectra, m/z: 361.1 for 1a (calculated *m/z*, 361.1); *m/z*: 375.2 for 2a (calculated *m/z*, 375.3) (Figure 2a (insert), S38); m/z: 373.1 for 4a (calculated m/z, 373.1) and m/z: 401.2 for 5a (calculated m/z, 401.1) (Figure S37, S39-S40). Also, they showed completely distinct cyclic voltammograms from their parent complexes (Figure S41). The solution state vibration (FT-IR) spectrum was measured for [Co^{III}(L2)(O₂)]⁺ 2a, exhibited O-O stretching frequency at 858 cm⁻ ¹, which is shifted to 816 cm⁻¹ while using $H_2^{18}O_2$ (90% atom purity) instead of H₂¹⁶O₂ (Figure 2b).^{17a} The observed isotopic shift ${}^{16}\Delta$ - ${}^{18}\Delta$ = 42 cm⁻¹ is almost closer to the calculated value of 51 cm⁻¹ for the O-O harmonic oscillator. In addition, Co-O₂ symmetric stretching of 2a was observed at 540 cm⁻¹ which is shifted to 523 cm⁻¹ while using H218O2, observed isotopic shift is ${}^{16}\Delta$ - ${}^{18}\Delta$ = 17 cm⁻¹ (${}^{16}\Delta$ - ${}^{18}\Delta_{(cal.)}$ = 21 cm⁻¹). The calculated vibrational frequency by DFT at 840 cm⁻¹ (O-O) and 511 cm⁻¹ (Co-O) are closer to experimental values (Figure 2b). These value are comparable to those of previously reported structurally and spectroscopically well-characterized side-on Co(III)-peroxo complexes such as [Co^{III}(Me₃-TPADP)(O₂)]⁺ (888 (Me₃-TPADP = 3,6,9-trimethyl-3,6,9-triaza-1(2,6)cm⁻¹) pyridinacyclo decaphane); [Co^{III}(12-TMC)(O₂)]⁺ (902 cm⁻¹) (12-TMC = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclodecane) and $[Co^{III}(13-TMC)(O_2)]^+$ (902 cm⁻¹) (13-TMC = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotridecane).^{6a-b} The isolation of single crystals of the cobalt(III)-peroxo species was unsuccessful with our great efforts. The direct reaction of 1a - 5a with benzene exhibited very lower yields phenol, 1a: 0.6%; 2a: 0.8%; 3a: 0.9; 4a: 0.7% and 5a: 0.3%. The observed phenol yields are extremely poor as compared to those in Table 1, which suggests that side-on Co(III)-peroxo type intermediate is unlikely to be involved in the benzene hydroxylation mechanism.



Figure 2. Electronic spectral changes for the reaction of **2** (4×10^{-4} M) with 2 equivalents NEt₃ and 10 equivalents of H₂O₂ at -40 °C in CH₃CN (a); ESI-MS of **2a** (insert). Vibrational spectra of **2a** in CH₃CN (b). The electronic spectral changes for the reaction of **2a** (4×10^{-4} M) with 3 equivalents HClO₄ at -25 °C in CH₃CN and ESI-MS (insert) (c). Vibrational spectra of **2b** in CH₃CN (d).

Further, the reaction of 3a with other substrates such as triphenylphosphine and thioanisole showed no oxygen atom transfer (OAT). This implies that species 3a is incapable of performing electrophilic OAT reactions as similar to the reports.6b,17b previous Whereas, substrate 2-phenyl propionaldehyde was converted into acetophenone (71%) (scheme 4) via deformylation pathway as similar to the previously reported side-on Co(III)-peroxo complexes $([Co^{III}(bbphc)(O_2)]^+, [Co^{III}(13-TMC)(O_2)]^+)$.^{17b-c} These results clearly indicate that the intermediates 1a - 5a likely side-on Co(III)-peroxo species, which are known to display nucleophilic character^{6b,17b-c} and do not facilitate benzene hydroxylation reactions under these conditions.

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The addition of 3 equivalents of H^+ (HClO₄) to **3a** in CH₃CN at -25 °C showed the spontaneous colour change from yellow to green, which possibly corresponds to [(L3)Co^{III}(OOH)]²⁺, **3b**. The formation was accompanied by the appearance of the characteristic LMCT (Ligand to Metal Charge Transfer) transitions at, 588 (ϵ , 350 M⁻¹ cm⁻¹) and 697 nm (ϵ , 437 M⁻¹ cm⁻¹ ¹) (Figure S42).¹⁸ ESI-MS spectra of the solution showed a peak at m/z = 266.8 accounts for $[(L3)Co^{III}(OOH)(CH_3CN)]^{2+}$ (calculated m/z = 266.62) (Figure S43), which is a prominent shift and distinct from 3a. This result indicates that 3a possibly converted into hydroperoxo species by H⁺ and this chemistry is well explored and its spectral signatures are comparable to the previous reports.^{6b,19} Similarly, hydroperoxo species [LCo^{III}(O-OH)]²⁺ of other complexes were generated by the reaction of respective side-on species with 3 equivalents of H⁺ at -25 °C in acetonitrile, which showed the identical characteristic spectral changes (Figure S44, S46, Table S8). Further they were confirmed by the observation of ESI-MS spectra of adducts $[(L)Co^{III}(OOH)(CH_3CN)]^{2+}$; **2b**: the calculated *m/z* = 208.58, Found m/z = 208.2) (Figure 2c, S47); 4b: the calculated m/z = 207.57, Found m/z = 207.1 and **5b**: the calculated m/z = 221.59, Found m/z = 221.6 (Figure S48 – S49), which are completely distinct mass pattern from their respective side-on species. Further, the addition of benzene to 2b and 3b at -25 °C in acetonitrile exhibited disappearance of bands at 587, 629 and 697 nm for 2b (Figure S50) and 588 and 697 nm for 3b (Figure S51). GC-MS analysis of the reaction mixture showed the formation of phenol. The solution state vibration (FT-IR) spectrum of the [L2Co^{III}(OOH)]²⁺ 2b is completely different from that of 2a, which exhibited two vibration modes at 832 cm⁻¹ (O-OH) and 564 cm⁻¹ (Co-O), which are shifted to 781 cm⁻¹ and 544 cm⁻¹ while using H₂¹⁸O₂ instead of H₂¹⁶O₂ (Figure 2d). Observed O-O vibrational frequency at 832 cm⁻¹ is comparable to that of a lowspin bleomycin-Co(III)-hydroperoxo complex (828 cm⁻¹).²⁰ This is good agreement with the calculated vibrational spectrum [784 cm⁻¹ (O-OH) and 536 cm⁻¹ (Co-O)] (Figure 2d). The isotopic shift of ${}^{16}\Delta$ - ${}^{18}\Delta$ = 51 cm⁻¹ (O-OH) and 20 cm⁻¹ (Co-O) are in closer agreement with calculated values of 49 cm⁻¹ and 26 cm⁻¹ respectively. These values are comparable to those reported for structurally and spectroscopically characterized Co(III)-OOH complexes such as low-spin bleomycin-Co(III)-hydroperoxo complex.²⁰ The isolated species **1a** - **5a** (5 μ M) were reacted with benzene in presence of three equivalents of H⁺ and showed phenol formation exclusively with yields of 1a (7%), 2a (9%), 3a (11), 4a (5%) and 5a (6%). However, the yields were enhanced while increasing the catalyst loading to 50 μ M, where yields of phenol, 1a: 22%; 2a: 25%; 3a: 27%; 4a: 15% and 5a: 17%. The observed phenol yields are almost identical to values in Table 1. The results are suggesting that benzene hydroxylation likely proceeds via $[LCO^{III}(O_2H)]^{2+}$ species rather $[LCO^{III}(O_2)]^+$ species. The involvement of [LCo^{III}(O₂H)]²⁺ species was further supported by the reaction of **3b** with triphenylphosphine and thioanisole. Wherein products were analyzed by GC-MS, showed formation of triphenylphosphine oxide (35%) and methyl phenyl sulfoxide (66%) respectively at 25°C over 3 h. So, it clearly suggests that the electrophilic nature of Co(III)-OOH

intermediate and facilitates the OAT reactions, A Scheme 4).^{6b,19b,19d} DOI: 10.1039/C9CY02601K



Scheme 4. Reaction pathway for Benzene hydroxylation.

The optimized geometry of **2** and its possible peroxo intermediates was optimized by DFT²¹ using LanL2DZ level (Figure S53) and TD-DFT calculations were performed using B3LYP 631-G (for C H N O) and LANL2DZ (for Co) basis sets. The total energy of $[(L2)Co^{||}(O_2)]^+$, $[(L2)Co^{||}(OOH)]^{2+}$ and $[(Co^{||}(L2))_2(\mu-O)_2]^+$ were calculated as 32016 eV, 32024 eV, and 59939 eV respectively. The TD-DFT results are comparable to the experimental electronic spectra of $[(L2)Co^{|||}(O_2)]^+$ and $[(L2)Co^{|||}(OOH)]^{2+}$, wherein the energy of peroxo to cobalt(III) LMCT (Ligand to Metal Charge Transfer) is closer to the experimentally observed values (415, 475, 505 nm and 390, 495 and 810 nm). (Figure S54).

Conclusion

The cobalt(II) complexes of 4N ligands were synthesized and structurally characterized as efficient catalysts for benzene hydroxylation. The molecular structures of complexes showed geometry in between square pyramidal and trigonal bipyramidal. The catalysts are found to be efficient and selective for hydroxylation of benzene to form phenol using H_2O_2 . The 29% yield of phenol with TON of 286 is attained without any over oxidized products, which is the highest catalytic efficiency reported for cobalt-based catalysts so far in the literature. The hydroxylation reaction apparently proceeds via cobalt(III)-OOH intermediates, which is established by the spectral methods and TD-DFT calculations. The KIE experiment results support the involvement of cobalt-bound oxygen species as a key intermediate. The isotope-labeling experiments indicate the H₂O₂ is the key oxygen supplier for phenol formation.

Experimental section

Materials

The chemicals homopiperazine, 3-(dimethylamino)-1-propylamine, 2-chloromethyl-4-methoxy-3,5-dimethylpyridine hydrochloride, 2-vinylpyridine, cobalt(II)chloride hexahydrate, sodium tetraphenylborate, nitrobenzene, tetrabutyl ammoniumhexafluorophosphate, benzene, toluene, chloroform-d, Benzene- d_6 , anisole, chlorobenzene, 2-phenyl

propionaldehyde(2-PPA) purchased from sigma Aldrich and $H_2^{18}O_2 - 90\%$ ¹⁸O atom were purchased from icon isotope. 2pyridinecarboxaldehyde, N, N-dimethylethylene diamine, sodium triacetoxyborohydride, Thianisole, triphenylphosphine was purchased from Alfa Aesar. Anhydrous acetonitrile, Dichloromethane, Hydrogen peroxide (30%) from Merck, India. Dry methanol, triethylamine, phenol were purchased from SD fine chemicals.

Physical Methods

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All workup procedures were carried out under ambient conditions. Electrospray Ionization Mass Spectra (ESI-MS) were measured on a Thermo LC-MS instrument. UV-Vis spectra were recorded on an Agilent 8453 spectrometer with a cooling unit by Unisoku (Osaka, Japan). FT-IR measurements were recorded using Thermo Nicolet 6700. Cyclic Voltammetry (CV) was performed using a three-electrode cell configuration. A platinum sphere (acetonitrile medium), platinum wire and Ag(s)/Ag⁺ were used as working, auxiliary and reference electrodes respectively. The tetrabutyl ammoniumhexafluorophosphate was used as a supporting electrolyte in acetonitrile. The $E_{1/2}$ values were observed under identical conditions for various scan rates. GC-MS and GC analysis performed on Agilent 5977E GCMSD using HP-5 MS ultra-inert (30 m × 250 μ m × 0.25 μ m) capillary column.

X-ray Crystal Structure Analysis

The experiment was performed on the Agilent Technologies Supernova-E CCD diffractometer. The suitable single crystals of 1, 2, 4, and 5 of suitable size were selected from the mother liquor and immersed in paraffin oil, then mounted on the tip of glass fiber. The structures were solved by direct methods using the program SHELXS-2013. Refinement and all further calculations were carried out using SHELXL-2013. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix leastsquares on F². CCDC 1954523, 1954536, 1954537 and 1954539 are containing the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via ww.ccdc.cam.ac.uk/data request/cif.

Synthesis of Ligands

Ligands N,N-Bis(2-pyridylmethyl)-N',N'-dimethylethane-1,2-diamine (L1), N,N-Bis(2-pyridylmethyl)-N',N'dimethylpropane-1,3-diamine (L2), N1,N1-bis((4-methoxy -3,5dimethylpyridin-2-yl)methyl)-N3,N3-dimethylpropane-1,3-

diamine (L3), 1,4-Bis[(pyridin-2-yl-methyl)]-1,4-diazepane (L4), 1,4-Bis[2-(pyridin-2-yl)ethyl]-1,4-diazepane (L5) synthesized using previously reported.⁷

Synthesis of Co(II) Complexes (1 - 5)

The Co(II) Complexes are prepared by known procedure⁸. To the solution of ligands (0.18 mmol) in methanol (10 mL), $CoCl_2 \cdot GH_2O$ (0.18 mmol) in methanol was added drop wise under stirring at room temperature. It was refluxed for 3 hours, subsequently the mixture was filtered and cooled to room temperature. Then, one equivalent of sodium tetraphenylborate/ sodium perchlorate in methanol was added, stirred for an additional hour. The complexes were precipitated as solid and then filtered and washed with Cold Methano P.2601K [Co(L1)Ci](Ph₄B) **1.** Isolated as green solid, yield = 61%. Analytically calculated elements for C₄₀H₄₂BN₄CoCl: C, 70.24; H, 6.19; N, 8.19 %. Found: C, 70.21; H, 6.17; N, 8.17 %. HR-ESI (*m*/*z*): Calculated for C₁₆H₂₂ClCoN₄ [M]⁺ 364.0865; Found. 364.0911. Diffusion of diethylether into acetonitrile solution of complex with perchlorate counter ion afforded single crystals suitable for X-ray analysis.

[Co(L2)CI](Ph₄B) 2. Isolated as purple solid, Yield = 77%. Analytically calculated elements for C₄₁H₄₄BN₄CoCl: C, 70.55; H, 6.35; N, 8.03 %. Found: C, 70.51; H, 6.32; N, 8.01 %. HR-ESI (m/z): Calculated for C₁₇H₂₄ClCoN₄ [M]⁺ 378.1021; Found 378.1012. Diffusion of diethylether into acetonitrile solution of complex afforded single crystals suitable for X-ray analysis.

[Co(L3)Cl](Ph₄B) 3. Isolated as purple solid, Yield = 57%. Analytically calculated elements for $C_{47}H_{56}BN_4CoO_2Cl$: C, 69.34; H, 6.93; N, 6.88 %. Found: C, 69.31; H, 6.91 N, 6.85 %. HR-ESI (*m/z*): Calculated for $C_{23}H_{36}ClCoN_4O_2$ [M]⁺ 494.1859; Found 494.1856.

[Co(L4)Cl](Ph₄B) 4. Isolated as purple solid, Yield = 49%. Analytically calculated elements for $C_{41}H_{42}BN_4CoCl: C, 70.75; H, 6.08; N, 8.05 %. Found: C, 70.71; H, 6.05; N, 8.03 %. HR-ESI ($ *m/z* $): Calculated for <math>C_{17}H_{22}ClCoN_4$ [M]⁺ 376.0865; Found 376.0925. Diffusion of diethylether into acetonitrile solution of complex with perchlorate counter ion afforded single crystals suitable for X-ray analysis.

[Co(L5)CI](Ph₄B) 5. Isolated as light blue solid Yield = 71%. Analytically calculated elements for $C_{43}H_{46}BN_4CoCl: C, 71.33; H, 6.40; N, 7.74 %.$ Found: C, 71.31; H, 6.37; N, 7.71 %. HR-ESI (*m/z*): Calculated for $C_{19}H_{26}ClCoN_4$ [M]⁺ 404.1178; Found 404.1229. Diffusion of diethylether into acetonitrile solution of complex afforded single crystals suitable for X-ray analysis.

General Procedure for Catalytic Hydroxylation Reaction

A catalytic amount of the [Co(L)Cl](Ph₄B) complex (5 μ mol, 0.1 mol%) was dissolved in acetonitrile (5.0 mL), benzene (5.0 mmol) and aqueous hydrogen peroxide (30%) (2.5 mL, 25 mmol) were introduced dropwise into the reaction solution over a period of 30 minutes. The mixture was stirred at 25 °C/60 °C for 5 hours. After cooling to room temperature, the catalyst was removed by passing through the silica-gel column. Then, a known amount of nitrobenzene was added as an internal standard. Conversion and yield of the reaction were determined with GC-MS/GC. No benzene oxidation products were detected in control experiments using the same experimental conditions but without the addition of a catalyst.

Determination of Kinetic Deuterium Isotope Effect

Benzene (2.5 mmol), benzene- d_6 (2.5 mmol), were added into a solution of [Co^{II}(L)CI]BPh₄ (**1** - **5**) (5.0 µmol) in acetonitrile (5 mL). An aqueous solution of hydrogen peroxide (30%) (25 mmol) was added directly under constant stirring over a period of 30 minutes. The mixture was stirred for 5 h at 60 °C. After cooling to room temperature, the complex was removed by passing through the solution on silica-gel column. The product distribution was determined by GC-MS. The kinetic isotope

effect (KIE) value for phenol production was calculated by (moles of phenol)/(moles of phenol- d_5).

Catalytic Hydroxylation reaction of benzene with $H_2^{18}O_2$

 $[{\rm Co^{II}(L3)CI}]{\rm BPh_4}$ (5 $\mu mol)$ (3) was dissolved into 3 mL acetonitrile, and benzene (0.12 mmol) and add ${\rm H_2^{18}O_2}$ (10 equivalent) into the reaction solution. The mixture was stirred 12 h at 60 °C. After cooling to room temperature, the cobalt complex was removed by passing through the silica-gel column. Then the reaction mixture was analyzed by GC-MS.

Catalytic Benzene Hydroxylation Reaction with H₂¹⁸O

The complex **3** (5 μ mol) was dissolved in H₂¹⁸O/acetonitrile (0.1 mL/1 mL). Benzene (0.5 mmol) and aqueous hydrogen peroxide (0.5 mL, 5 mmol) were slowly introduced into the solution. The reaction mixture was stirred at 60 °C for 5 h. After cooling to room temperature, the cobalt complex was removed by passing through the silica-gel column, the products were analyzed by GC-MS.

Catalytic Hydroxylation of substituted benzene

The most active catalyst **3** (5 μ mol) was dissolved in acetonitrile (5.0 mL). Substrate (5.0 mmol) and 30% of hydrogen peroxide (2.5 mL, 25 mmol) were slowly added into the solution over a period of 30 minutes. The reaction mixture was stirred at 60 °C for 5 hours. After cooling to room temperature, the cobalt complex was removed by passing through the silica-gel column, the products were analyzed by GC-MS/GC.

Kinetic Measurement

Kinetic experiments for the formation of $[Co^{III}(L)(O_2)]^+$, $[Co^{III}(L)(OOH)(CH_3CN)]^{2+}$ complex was carried out in a 1 cm path length UV-visible cell on a Unisoku thermostated cell holder designed for low-temperature measurements. The deaerated solution of the cobalt complexes **1** - **5** (4 × 10⁻⁴ M) in the cell was kept at the desired temperature for several minutes and aqueous 30% H₂O₂ (10 equivalent) was added from a microsyringe in the presence of two equivalent of triethylamine in acetonitrile at -40°C /25 °C. The formation of the $[Co^{III}(L)(O_2)]^+$ intermediates was monitored by UV-visible, FT-IR and ESI-MS. Further, $[Co^{III}(L)(O_2)]^{2+}$ species were treated with 3 equivalent HClO₄ to generate $[Co^{III}(L)(OCH)]^{2+}$ intermediate and monitored.

The species $[Co^{III}(L)(OOH)(CH_3CN)]^{2+}$ was freshly generated from $[Co^{III}(L)(O_2)]^{2+}$ and 3 equivalents of $HCIO_4$ at -25 °C in acetonitrile. After, the substrate benzene was added via microsyringe into the solution. The reaction was carefully monitored and the reaction mixture was passed through a silica column and the formation of phenol was confirmed by GC-MS/GC.

Solution FT-IR Measurement

Solution FT-IR measurements were recorded for freshly generated $[Co^{III}(L)(O_2)]^{2+}$ and $[Co^{III}(L)(OOH)(CH_3CN)]^{2+}$ species, which were transferred into the CaF₂ cell *via* microsyringe and then spectra were measured.

Calculation of Steric Maps

The steric r	naps were ob	tained us	ing the Sa	ambVca 2.1A	A web
application,	which	can	be	found	at

https://www.molnac.unisa.it/OMtools/sambvca2.1/index.html 11 DOI: 10.1039/C9CY02601K

DFT Methods

The geometry optimizations were performed using density functional theory (DFT) methods. For the metal ion involving systems, the LANL2DZ basis sets with the Becke3–Lee–Yang–Parr hybrid functional (B3LYP) were used, while the 6-311G (d) basis sets were used for elements other than metals. All DFT calculations were carried out by using the Gaussian 09 program package.²⁰

Conflicts of interest

"There are no conflicts to declare".

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Single-Step Benzene Hydroxylation by Cobalt(II) Catalysts via Cobalt(III)-Hydroperoxo Intermediate

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Cobalt(II) complexes are reported as the efficient and selective catalysts for single-step phenol formation from benzene using H_2O_2 . The catalysis proceeds likely *via* the cobalt(III)-hydroperoxo species.

