Aromaticity Driven Electrocatalytic Water Oxidation by a Phosphorus-Nitrogen PN³-Pincer Cobalt Complex

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ABSTRACT: Water oxidation is the primary step in both natural and artificial photosynthesis to convert solar energy into chemical fuels. Herein, we report the first cobalt-based pincer catalyst for electrolytic water oxidation at neutral pH with high efficiency under electrochemical conditions. Most importantly, ligand (pseudo)aromaticity is identified to play an important role in the electrocatalysis. A significant potential jump (~ 300 mV) was achieved towards a lower positive value when the aromatized cobalt complex was transformed to a (pseudo)dearomatized cobalt species. This complex catalyzes the water oxidation in its high valent oxidation state at a much lower overpotential (~ 340 mV vs. NHE) based on the onset potential (0.5 mA/cm²) of catalysis at pH 10.5, outperforming all the other literature systems. These observations may provide a new strategy for the design of earth-abundant transition metal-based water oxidation catalysts.

Oxygen evolution reaction (OER) represents the bottleneck for practical hydrogen generation needed for the conversion of solar/electrical energy into chemical fuels for storage and transportation (2, 9, 20, 37). Recent literature has seen rapid expansion in research in the area of water oxidation (19, 28). In particular, the development of non-noble metal based catalysts that can catalyze water oxidation efficiently has taken center stage. Heterogeneous water oxidation catalysts (WOCs), such as transition metal-oxides (29, 33) and mixed-metal oxides (5, 26, 30, 41), have traditionally been used as anodes (49), and recent discoveries of cobalt-phosphate, cobalt-acetate, and related catalysts have generated some very exciting catalysts (15, 27, 40). Besides metal oxide based heterogeneous catalysts, bio-inspired catalysts have also received much attention (4, 21, 38). Molecular catalysts are amenable to change in ligand design and can be judiciously armed with functionalities to control the overpotential and enhance the rate (3, 8, 44). A significant number of WOCs have been established based on mononuclear and multinuclear transition metal complexes including Mn, Fe, Co, Cu, Ru, and Ir (10-13, 16, 42, 47, 52), and a series of cobalt complexes with different ligands have been examined for electrochemical water oxidation (1, 10, 11). However, most of the catalysts are unstable under highly oxidizing conditions required to oxidize the metal and often decompose to form nano-particles (34, 39, 43, 45, 46). Robustness of the ancillary ligand is thus key to the stability of WOCs, and search for new ligand platforms is an ongoing challenge.

Pincer-type complexes have been used abundantly in organometallic chemistry (18, 22, 24, 25, 31, 35). Among them, the ligand aromatization and dearomatization of a series of pyridine-based pincer compounds have been demonstrated to be an efficient and unique strategy to dynamically control the ligand properties (Fig. 1) (18, 36, 51). Accordingly, a wide range of dehydrogenation and hydrogenation reactions were developed (6, 7, 17, 23, 32, 50). Moreover, we have also witnessed the enhanced thermodynamic stability in our $\text{PN}^3(\text{P})$ system (14). As the dearomatized ligands are better donors that may stabilize the oxidized states of metal while the aromatized counterparts are weaker ones that may favor the reduced metals, it is our intuition that such a aromatization/dearomatization process can be utilized to mediate and control redox reactions. In this manuscript, we report a cobalt-based homogeneous WOC supported by a cooperative PN^3 ligand. This catalyst is electrochemically proficient of evolving O_2 from neutral aqueous medium (pH 7 phosphate buffer) at room temperature. More importantly, we have demonstrated for the first time that the metal-ligand cooperation via aromatization-dearomatization plays a crucial role

for controlling reactivity during water splitting. The (pseudo)dearomatized complex catalyzes the water oxidation in its high valent oxidation state at a much lower overpotential. This work emphasizes the exploitation of design principle to circumvent the technical challenges.

Fig. 1. Schematic representation of metal-ligand cooperativity. Metal-ligand cooperation by aromatization and dearomatization of the central pyridine ring (highlighted in blue) plays a crucial role in various bond activation and catalysis.

Results and Discussions

Synthesis and Characterization. The N-(di-tert-butylphosphino)-[2,2'-bipyridin]-6-amine ligand (L^{PN3}) was synthesized according to literature procedure (7). The pincer ligand was coordinated to $CoBr_2$ in THF, and the desired Co^{II} complex (**1**) was obtained upon exposure in air. While Complex **1** crystallizes in primitive centrosymmetric orthorhombic *Pbca* space group, the (pseudo)dearomatized structure crystallizes in orthorhombic *Pnma* space group. Single-crystal x-ray diffraction analysis of both aromatized and (pseudo)dearomatized structures of **1** revealed five-coordinated Co (II) complexes comprising of two N atoms from bipyridine skeleton and one O atom of oxidized phosphine arm of the ligand moiety with different N3-C10 distances (1.321 and 1.390 Å for the aromatized and (pseudo)dearomatized form, respectively, Fig. 2a-b). This complex was also characterized by ESI-MS and 1H NMR spectroscopy (*SI Appendix*, Fig. S1-S2, Table S1-S2).

Fig. 2. Crystal structure of (a) aromatized and (b) (pseudo)dearomatized crystal structure of complex **1**. Atoms are shown in 50% probability ellipsoid model. All the hydrogen atoms except one from N-H moiety have been omitted for clarity.

UV-Vis absorption spectroscopy. Complex **1** exhibits two bands, a major peak at 410 nm, and another small peak at 335 nm in DMF (Fig. 3a). Upon addition of one equivalent of base (KO^tBu) in DMF solution, only one peak at 410 nm arises due to the formation of (pseudo)dearomatized species. The addition of three equivalent of acid (PTSA) and water shifts the equilibrium towards aromatized species and only a band at 335 nm is observed (Fig. 3b). The appearance of these two peaks is reversible depending on addition of base and acid. The spectroscopic data are consistent and support the acid-base equilibrium between aromatized and (pseudo)dearomatized species in DMF at room temperature (Scheme 1). The equilibrium between these two species is also exhibited in aqueous medium. As the aromatized complex shows band at 330 nm in water and pH (7-10) phosphate buffer that is shifted to 370 nm in basic medium above pH 10.5 buffer due to the formation of (pseudo)dearomatized form of complex **1** (Fig. 3c).

Fig. 3. UV-Vis absorption spectroscopy and showing acid-base equilibrium of 1. (a) UV-vis titration using base and acid in DMF. (b) UV-vis titration using water and base in DMF; (c) in different buffer media (phosphate buffer).

Scheme 1. Predominant structure of complex 1 in different solvents.

Cyclic voltammetry. The Co complex exhibits two irreversible oxidation processes in the positive potential range in DMF under an argon atmosphere. As the (pseudo)dearomatized Co complex predominates in DMF at room temperature, the oxidation potential at 0.95 V ($E_{p,a}$) vs Ag/AgCl/1M KCl corresponds to oxidation of Co^{III} to Co^{IV} for the (pseudo)dearomatized cobalt complex and the oxidation potential at 1.16 V ($E_{p,a}$) is responsible for the aromatized cobalt complex which appears after addition of 3 eq PTSA in DMF solution (Fig. 4a). One broad irreversible CV feature is obtained around 0.19 V ($\Delta E_p = 120$ mV) corresponding to Co^{III/II} reduction wave (*SI Appendix*, Fig. S3A). The CV corresponding to all the redox processes is

recorded at different scan rates and shows a linear relationship with the square root of scan rate ($v^{1/2}$), which confirms a diffusion-controlled process under these conditions (*SI Appendix*, Fig. S3B-C). Upon gradual addition of water to a DMF solution of the complex **1** reveals a positive shift of anodic peak potential, consistent with the formation of high valent cobalt aromatized species and the anodic current gradually increases at 1.3 V vs. Ag/AgCl/1 M KCl, specifying an electrocatalytic water oxidation process (Fig. 4b).

Fig. 4. (a) Cyclic voltammograms of complex **1** (1.0 mM) in degassed dry DMF solution, after addition of acid (PTSA) under an argon atmosphere with 0.1 M $n\text{Bu}_4\text{NPF}_6$ as a supporting electrolyte. (b) Electrocatalytic water oxidation in DMF solution upon gradual addition of H_2O . Glassy carbon (GC, diameter 3 mm) was used as a working electrode, Pt-wire as a counter electrode, Ag/AgCl/1M KCl as a reference electrode at a scan rate of 50 mV/s.

Electron Paramagnetic Resonance (EPR). The X-band EPR spectrum of complex **1** at 10 K showed that the cobalt center exists in its high-spin ($S = 3/2$) ground state in both DMF and water solution. The five coordinated aromatized and (pseudo)dearomatized Co^{II} complex show characteristic EPR spectra, e.g. an axial signal with g_{eff} -value of 4.49 and rhombic signal with two component at 4.93 and 4.23 in a mixture of DMF along with 3eq PTSA and DMF, respectively (*SI Appendix*, Fig. S4A-B).

Electrochemical Catalysis. The electrochemical properties for OER of complex **1** are investigated in 0.1 M phosphate buffer solution using 0.5 mM catalyst concentration. On scanning at 50 mV/s from 0 to 1.6 V, a strong electrocatalytic current with an onset potential of 1.3 V vs. NHE appears in the cyclic voltammogram (CV) at pH 7.0 phosphate buffer solutions (Fig. 5a, red line). Two irreversible oxidation processes were observed, one at $E_{p,a} = 1.2$ V (with slight current enhancement) (Fig. 5a, inset) and a large irreversible current at 1.48 V ($E_{p,a}$) vs. NHE. The first anodic wave is assigned as the $1e^-$ oxidation, later one shows much larger current in the irreversible water oxidation process indicating electrocatalysis. The water oxidation is absent for blank GC electrode in pH 7 phosphate buffer without catalyst (Fig. 5a, violet line). The catalytic current exhibits a linear dependence on the catalyst concentration consistent with single site cobalt catalysis (Fig. 5b). The overpotential of the catalytic oxygen evolution (onset potential is 1.3 V vs. NHE at 0.5 mA/cm² current density) in pH 7 phosphate buffer for Co complex **1** is ~0.48 V (the thermodynamic potential for water oxidation at pH 7 is 0.82 V vs. NHE); the value is comparable to the earlier reported efficient molecular cobalt catalysts. This catalyst works with an exchange current density (j) of 5.3 mA/cm² which is better than some of the heterogeneous catalyst, such as RuO_x and IrO_x (33).

Fig. 5. (a) Cyclic Voltammetry diagrams of 0.5 mM complex **1** (red line) and blank electrode without catalyst (violet line) under the same conditions using glassy carbon working as well as counter electrode and Ag/AgCl/1M KCl reference electrode at a scan rate of 50 mV/s in 0.1 M pH 7 phosphate buffer. (b) CVs of different concentration of complex **1** in 0.1 M phosphate buffer at pH 7.0 (inset: linear regression of i_{cat} vs. catalyst concentration, $[C_{cat}]$).

Scheme 2. The aqueous speciation of the Cobalt complex, observed by electrochemistry, consistent with UV-vis.

Electrocatalytic pH dependent investigation. The electrochemical behavior of complex **1** was studied over a wide range of pH values from 5 to 11 in 0.1 M phosphate buffer solutions (Fig. 6a). Above pH 10, a substantial potential jump (~ 300 mV) with respect to onset as well as peak potential was observed towards a lower value and the peak potential of large electrocatalytic current at pH 10.5 coincide with the anodic peak potential of CV in DMF under this conditions, suggesting the aromatized cobalt complex was transformed to a (pseudo)dearomatized cobalt complex at a pH above 10 (Fig. 6b). This jump is consistent with the pK_a observed for complex **1**. Therefore, these results establish a key role of the aromaticity of the pincer complex towards lowering of overpotential (~ 140 mV vs. NHE) at higher pH values (above 10) for electrocatalytic water oxidation. The (pseudo)dearomatized cobalt complex formed above pH 10 catalyzes the water oxidation in its high valent oxidation state at a much lower overpotential (~ 340 mV vs. NHE) based on the onset potential (0.5 mA/cm^2) of catalysis at pH 10.5 (Scheme 2).

Fig. 6. (a) Overlay of cyclic voltammograms in different pH buffer solutions (pH 5-11) at a scan rate of 50 mV/s. (b) Overlay of cyclic voltammograms in different buffer solutions (pH 7-10.5) with CV of **1** in DMF

solution using 0.5 mM catalyst under homogeneous condition. Glassy carbon (GC, diameter 3 mm) was used as both working and counter electrode, Ag/AgCl/1M KCl reference electrode and 0.1 M tetrabutyl ammonium perchlorate as supporting electrolyte.

Water oxidation kinetics. The S-Shaped of the waves indicates that the catalytic current is affected by both substrate diffusion and the kinetics of the catalytic reaction under these conditions (Fig. 7a). The catalytic current (i_{cat}) is linearly dependent on the bulk concentrations of catalyst (Fig. 5b, inset). The limiting catalytic current should follow the relationship displayed in equation (1), where k_{cat} is the effective first-order rate constant (TOF), A is the electrode surface area (0.07 cm^2), F is Faraday's constant, C_{cat} is the catalyst concentration, $n_c=4$, is the number of electrons transferred in each catalytic cycle and D is the diffusion coefficient of the catalyst.

$$i_{\text{cat}} = n_c F A C_{\text{cat}} (D k_{\text{cat}})^{1/2} \dots\dots\dots (1)$$

scan rate dependent CVs shows that the first irreversible oxidation wave is diffusion limited at the electrode. The peak current (i_d) varies linearly with $v^{1/2}$, which is consistent with the Randles-Svecik equation described in equation (2) (*SI Appendix*, Fig. S5), where $n_d=1$, is the number of electrons transferred in the non-catalytic wave, $\alpha=0.5$ is the transfer coefficient of the catalyst, and v is the scan rate.

$$i_d = 0.496 n_d F A \alpha^{1/2} C_{\text{cat}} (n_d F v D / RT)^{1/2} \dots\dots\dots (2)$$

By dividing Eq. 1 by Eq. 2, a relationship between i_{cat} and i_d is obtained in eq. 3, and the first order rate constant for water oxidation can be estimated using this equation.

$$i_{\text{cat}}/i_d = 0.359 n_c / n_d^{3/2} (k_{\text{cat}} / \alpha v)^{1/2} \dots\dots\dots (3)$$

A linear correlation of i_{cat}/i_d vs $1/v^{1/2}$ is obtained and the k_{cat} , is calculated from the slope to be 402 s^{-1} for the aromatized cobalt complex of **1** at pH 7 (Fig. 7b). A similar approach is applied for the (pseudo)dearomatized complex, (i.e. above pH 10) and the calculated TOF is 28 s^{-1} at pH 10.5 (*SI Appendix*, Fig. S6). The remarkable activity of this catalyst compares well with those reported for the best cobalt-based WOCs (Table 1) (10, 11, 44, 46, 48).

Fig. 7. (a) CVs of complex **1** at different scan rates in 0.1M pH 7 phosphate buffer.(inset: the data is showing i_d current, $1e^-$ oxidation current); (b) The plot of i_{cat}/i_d vs $1/v^{1/2}$ where the blue line represents the best linear fit in pH 7. (c) Bulk electrolysis of 0.75 mM Co complex **1** on graphite rod electrode ($A = 1 \text{ cm}^2$) at 1.35 V and 1 V vs Ag/AgCl in pH 7 and pH 10.5 buffer, respectively.

Table 1. Comparison of electrochemical water splitting overpotential (η), turn over frequency (TOF), turn over number (TON) with reported homogeneous catalysts.

Catalyst	η	TOF (s^{-1})	TON	Reference
$[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_4\text{O}_{34})_2]^{10-}$	350 mV	5 (at pH 8)	75	Hill et al., Science 2010
$\text{CoH}^{\text{BF}}\text{CX}-\text{CO}_2\text{H}$	600 mV	0.81(pH 7)	-	Nocera et. al., JACS, 2011
$[\text{Co}(\text{Py}_5)(\text{OH}_2)](\text{ClO}_4)_2$	500 mV	79 (pH 9.2)	-	Berlinguette et al., Chem. Comm., 2011
$\text{Na}[\text{TAML}]\text{Co}^{\text{III}}$	380 mV	9 (pH 7)	-	Zhang et al., JACS, 2018
$\text{Co}^{\text{II}}\text{-TDMIImP}$	580 mV	1400 (pH 7)	-	Groves et al., PNAS, 2013
Complex 1 (pH 7)	480 mV	402 (pH 7)	54	This work
Complex 1 (pH 10.5)	340 mV	28 (pH 10.5)	79	This work

Proof of homogeneous catalysis and calculation of turn over number (TON). O_2 evolution was confirmed by GC after controlled potential electrolysis at 1.3 V vs. Ag/AgCl at pH 7 phosphate buffer at room temperature (Fig. 7c). To further characterize the electrocatalytic process, bulk electrolysis was performed at two different potentials at 1.35 V and 1 V vs. Ag/AgCl for the aromatized and (pseudo)dearomatized Co complex, respectively, under the same conditions, and the data suggest that O_2 was generated under conditions. Electrodes after multiple CVs gave no catalytic current in a fresh, cobalt-catalyst-free electrolyte at pH 7.0 (described in the method section). A faradaic efficiency greater than 88% was estimated from the gas collected over 20

minutes of electrolysis at pH 7 and 45 minutes of electrolysis at pH 10.5 (see supporting information). Absorption spectra of the solution before and after electrolysis indicates 16% and 9.6% decomposition of the catalyst, respectively (*SI Appendix*, Fig. S7). The TON is thus determined to be 54 and 79 at pH 7 and 10.5, respectively, suggesting that this cobalt complex is relatively robust as a fast, water soluble water oxidation homogeneous catalyst. Taking these observations into account, the studies provide the key role of aromaticity towards stability in the homogeneous electrocatalytic process under the conditions used here. Control potential electrolysis of complex **1** using both Hg-pool (20 cm²) and graphite electrode (1 cm²) indicates that the complex is stable through the course of the electrolysis at pH 7.0.

Conclusions

In summary, electrochemical water splitting exhibited by a PN³-pincer cobalt catalyst under homogeneous conditions is demonstrated. Most remarkably, upon ligand dearomatization at pH 10.5, a significant potential jump was observed towards a lower positive value, making this Co system substantially more energy efficient. The TONs of 54 and 79 at pH 7 and 10.5, respectively, suggest that this PN³-Co complex is relatively robust as a fast water soluble water oxidation homogeneous catalyst. Moreover, manipulating the activity of water oxidation by controlling the ligand aromaticity shall open up new approaches for the development of efficient electrocatalytic systems.

Methods

Materials. All the chemical reagents and solvents were of analytical grade and were used as received from sigma Aldrich suppliers without any further purification. All the organic solutions were prepared in the glove box. Synthesis of PN³ ligand were performed under an argon atmosphere. Ligand purification was done by flash chromatography using Merck silica gel 60. PN³-Co complex was synthesized in air at room temperature. All the aqueous phosphate buffer solutions were prepared using ultrapure deionized water at 23 °C (Milli-Q).

Synthesis and Characterization of Aromatized PN³-Co complex. PN³ ligand was synthesized according to literature report. 200 mg of PN³ ligand (0.63 mmol) was weighed in a round bottom flask along with CoBr₂ (140 mg), 15.0 ml of THF was added, and the solution was stirred for overnight at room temperature. Greenish product insoluble in THF was obtained after filtering off the solvent. It was then washed with THF. Crystallization was done for the aromatized complex by dissolving solid product in DMF/ACN (0.5:9.5) mixture and slow diffusion into pentane layer to obtain blue Crystal. The ¹H NMR spectrum of **1** collected in DMSO-d₆ exhibits significantly broadened signals, suggesting that the generation of a paramagnetic cobalt compound (Supplementary Fig. 1).

Blue crystal; 70% yield. ¹H NMR (500 MHz, D₆DMSO): 89.64 (1H), 58.60 (1H), 53.2 (1H), 38.7 (1H), 22.4 (2H), 2.65 (18H), -38.83 (1H); HRMS (ESI): Calcd for C₁₈H₂₆Br₂CoN₃OP, m/z 549.95, Found

469.03 (M-Br)⁺. Anal. Calcd for C₁₈H₂₆Br₂CoN₃OP: C, 39.30; H, 4.76; N, 7.64. Found: C, 39.20; H, 4.80; N, 7.60.

Synthesis of (pseudo)dearomatized PN³-Co complex. To a solution of **1** (50 mg, 0.09 mmol) in 10 mL of dry DMF in glovebox at room temperature was added cobaltocene (17.2 mg, 1.00 equiv), and the solution was stirred for 1 h. The solvent was removed under vacuum. Then, the solid was dissolved in acetonitrile and filtered through a small Celite plug and concentrated under reduced pressure to afford a green solid (yield ~90%). Crystallization was done by dissolving solid product in ACN and slow evaporation to obtain green Crystal. Complex show broadened signals in ¹H NMR.

Physical Characterization. X-ray quality crystals were immersed in cryo-oil, mounted in a Nylon loop and measured at 130 K. Intensity data were collected using a Bruker D8 Venture SMART CCD diffractometer with graphite monochromated Mo-K α (λ = 0.71073 Å) radiation. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all the observed reflections. Data were corrected for absorption effects using the multi-scan method (SADABS). Structures were solved by direct methods by using the SHELXS-2016 package and refined with SHELXL-2016.

¹H, spectra were recorded using Bruker AVIII 500 spectrometer. EPR spectra was recorded using X-band continuous wave Bruker EMX PLUS spectrometer (BrukerBioSpin, Rheinstetten, Germany) equipped with standard resonator for high sensitivity CW-EPR operating with a microwave frequency. The absorption spectra were measured in an Agilent technologies (serial no. - CN22808243). Chemical shifts in ¹H NMR was reported in parts per million (ppm). High resolution mass spectroscopy was performed at the KAUST analytical core lab. Elemental analyses were performed at the KAUST analytical core lab using a Flash 2000dThermo Scientific CHNS Analyzer.

Electrochemical Experiments. All electrochemical experiments were performed using a CH Instruments with a model number VMP3 s/n: 0512 (Bio-Logic SAS). The Cyclic Voltammetry (CV) data are collected under anaerobic condition under argon atmosphere in DMF. A Pt wire electrode was used as a counter electrode. The measurements were made against a leak proof Ag/AgCl/1M KCl aqueous reference electrode. The Glassy Carbon electrode (0.07 cm²) was used as working electrode which was freshly polished to get rid of all the contaminations out before each single use.

The catalyst solution (1 mM anaerobic solution in DMF) with 0.1 M tetrabutylammonium hexafluorophosphate was taken in a four neck electrochemical cell which was degassed by Ar gas before electrochemical experiment. H₂O was added slowly into the solution, and then the electrochemical data was collected. 0.5 mM concentration of catalyst in pH 7 aqueous phosphate buffer solution was taken for electrocatalytic water oxidation. The electrochemical investigation was performed in a wide range of pH (5-11).

The bulk electrolysis experiments of complexes were performed in a four-neck glass vessel (volume 10 mL including the headspace) where three of the necks were occupied with a coiled Pt wire as counter electrode, Ag/AgCl (in saturated KCl) as a reference electrode, and a carbon rod (surface area 1.0 cm²) as working electrode, respectively. The last of the necks was connected with inverted burette through channel. Controlled potential electrolysis (CPE) was done at the respective potential vs Ag/AgCl.

Homogeneity Test. The rinse test of the complex **1** was performed to figure out the nature of the catalyst; i.e., whether it is heterogeneous or homogeneous. For this purpose, we have performed three consecutive runs for each sample. In the first run, a complete scan was recorded for the complex in water where catalytic event was observed. Then, the glassy carbon electrode (working electrode in this case) was thoroughly rinsed with water and polished with 0.25 μ m alumina powder to remove any possible heterogeneous species formed on the electrode surface. Afterward, a second run was performed in the same solution containing the complexes with the cleaned electrode. Here, this second run was stopped at a positive potential, close to the potential where the maximum catalytic current was observed. Then, the working electrode was only rinsed with water (no polishing with alumina) and a third run was recorded in a fresh

catalyst free electrolytic solution. As the third run did not exhibit any catalytic current compared to the first two runs, it concluded that the catalytic current is generated due to homogeneous catalytic pathway.

Confirmation of Oxygen Evolution. O₂ evolution was guaranteed by controlled potential electrolysis at 1.3 V vs. Ag/AgCl at pH 7 phosphate buffer at room temperature. Headspace gas analysis was performed by gas chromatography (GC) fitted with thermal conductivity detector (TCD) in a sealed electrochemical cell containing 0.75 mM solution of complex **1**, graphite rod working electrode with a large surface area (1 cm²), platinum counter electrode and Ag/AgCl/1M KCl reference electrode. Here, we performed electrolysis at a fixed potential for a certain period under conditions similar to those mentioned above and obtained substantial O₂ that was confirmed by gas chromatograms (GC). The certain amount of H₂ was also detected along with O₂ in the gas collected after bulk electrolysis in GC. To further characterize the electrocatalytic process, bulk electrolysis was performed at two different potentials which are 1.35 and 1 V vs. Ag/AgCl for the aromatized and (pseudo)dearomatized Co complex, respectively, under same conditions and the data suggest that the complex **1** produced both O₂ and H₂ in both the pHs.

Faradaic Yield, TOF and TON Calculation.

Faradaic Yield Calculation.

FY is determined by the equation

$$\text{FY (\%)} = 100 * \text{Amount of O}_2 \text{ produced (mole)} / (\text{Amount of charge consumed during BE} / F * 4)$$

During the Constant Potential Electrolysis (CPE) in pH 7 buffer at 1.35 V vs Ag/AgCl/1M KCl, total charge consumed was 30 C in 1200 sec and 4.60 ml mixture gas (O₂ and H₂) was collected in an inverted burette set up connected to electrochemical cell through a channel.

Hence, no. of moles of O₂ produced = 4.60/3*22400 mole

Therefore, Faradaic Yield (FY) = 88.09%.

TOF Calculation.

Here, we get the slope (m) = 40.75 in pH 7 buffer (Supplementary Fig. 7b)

$$\text{Therefore, TOF}_{\text{max}} = 40.75^2 / (0.359 \times 4)^2 * 1^3 * 0.5 = 402 \text{ s}^{-1}$$

Again, Slope (m) = 10.69 in pH 10.5 buffer (supplementary Fig. 6)

$$\text{TOF}_{\text{max}} = 10.69^2 / (0.359 \times 4)^2 * 1^3 * 0.5 = 28 \text{ s}^{-1}$$

TON Calculation.

TON = (Total no. of moles of O₂ produced / Total no. of moles of catalyst used)

At 1.35 V vs Ag/AgCl/1M KCl (pH 7 phosphate buffer)

During bulk electrolysis (BE) using graphite electrode amount of O₂ collected is 1.53 ml *i.e.* 1.53/22400 moles.

During BE, 10 ml 0.75 mM solution was used and after 20 minutes of electrolysis decay of the catalyst was 16.4%.

The complete decay will take 122 minutes. The decay has been calculated from the concentration of the catalyst before and after electrolysis from the absorbance measured in UV-visible spectroscopy.

$$\text{Now, TON} = (1.53/22400) * (10^3 / 0.75 * 10^{-3} * 10) * (122/20) = \sim 54$$

At 1 V vs Ag/AgCl/1M KCl (pH 10.50 phosphate buffer)

During bulk electrolysis (BE) using graphite electrode amount of O₂ collected is 1.4 ml *i.e.* 1.4/22400 moles.

For this process, 11 ml 0.75 mM solution was used and after 45 minutes of electrolysis decay of the catalyst was ~9.6%. The complete decay (100%) will take 469 minutes.

$$\text{TON} = (1.40/22400) * (10^3 / 0.75 * 10^{-3} * 11) * (469/45) = \sim 79$$

Therefore, TON at 1.35 V (pH 7) and 1 V (pH 10.50) (vs Ag/AgCl/1M KCl) are 54 and 79, respectively.

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Author contributions

P.K.D., S.B. and A.R. undertook electrochemical experiments. P.K.D, A.D., and K.-W.H. analyzed and interpreted data, and wrote the paper. P.K.D and P.C. performed XRD analysis. S.B. conducted O₂ detection. K.-W.H. conceived and directed the project.

Competing interests

The author declare no competing interests.

Additional information

Supplementary information is available for this paper.

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Figure S1. ^1H NMR of the complex **1** in DMSO-d_6 .

A. ESI-MS (positive) spectra of complex **1** in DMF

B. ESI-MS (positive) spectra of complex **1** in water

Figure S2. Electrospray ionization mass spectra (ESI-MS positive) of the complex **1**.

Table S1. Crystallographic data for aromatized and pseudodearomatized structure of complex **1**.

Parameters	Aromatized Structure	pseudodearomatized Structure
empirical formula	C ₁₈ H ₂₆ N ₃ OPBr ₂ Co	C ₂₈ H ₂₉ N ₃ OPBr ₂ Co ₂
fw	550.14	732.19
crystal system	Orthorhombic	Orthorhombic
space group	<i>Pbca</i>	<i>Pnma</i>
<i>a</i> (Å)	13.199(3)	15.2020(9)
<i>b</i> (Å)	16.218(3)	9.2788(6)
<i>c</i> (Å)	20.017(4)	20.8564(13)
α (deg)	90.00	90
β (deg)	90.00	90.00
γ (deg)	90.00	90
<i>V</i> (Å ³)	4284.8(15)	2941.9(3)
<i>Z</i>	8	4
<i>T</i> (K)	100(2)	120(2)
2θ (deg)	4.07–51.97	4.80–74.58
<i>D</i> _{calcd} (g cm ^{−3})	1.706	1.653
<i>F</i> (000)	2200	1460
Absorption-correction	Multi-scan	Multi-scan
Index ranges	−16 ≤ <i>h</i> ≤ 16 −19 ≤ <i>k</i> ≤ 19 −24 ≤ <i>l</i> ≤ 24	−25 ≤ <i>h</i> ≤ 25 −15 ≤ <i>k</i> ≤ 15 −35 ≤ <i>l</i> ≤ 35
<i>R</i> _{int}	0.0747	0.0677
Goodness-of-fit on <i>P</i> ²	1.167	1.051
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0337/0.1318	0.0374/0.1241
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b [for all <i>F</i> _o ²]	0.0434 /0.1415	0.0512/0.1390

Table S2. Bond lengths and angles in aromatized and pseudodearomatized structure of complex **1**.

Parameters	Aromatized structure	pseudodearomatized structure
P=O	1.498(3)	1.5191(18)
C10-N3	1.391(6)	1.324(3)
Co1-O1	1.979(3)	1.9875(17)
Co1-N1	2.075(4)	2.108(2)
Co1-N2	2.181(4)	2.0957(19)
Co1-Br1	2.5277(8)	2.5055(3)
Co1-Br2	2.4355(8)	-
O1-Co1-N1	131.82(14)	174.34(7)
O1-Co1-N2	84.17(13)	96.85(7)
N1-Co1-N2	77.12(14)	77.49(8)
O1-Co1-Br1	88.39(9)	95.76(3)
N2-Co1-Br1	166.35(9)	119.466(13)
N1-Co1-Br1	99.71(11)	87.14(3)
Br1-Co1-Br1A/Br2	105.36(3)	117.693(16)
Br1A/Br2-Co1-N1	99.52(10)	87.14(3)
Br1A/Br2-Co1-N2	88.28(9)	119.465(13)
Br1A/Br2-Co1-O1	124.09(10)	95.76(3)

Figure S3. Cyclic voltammograms of complex **1** (1.0 mM) (A) at a scan rate of 20 mV/s and (B) at different scan rate in dry degassed DMF solution under an argon atmosphere with 0.1 M $n\text{Bu}_4\text{NPF}_6$ as a supporting electrolyte. Glassy carbon (GC, diameter 3 mm) was used as a working electrode, Pt-wire as a counter electrode, Ag/AgCl/1M KCl as a reference electrode; (C) Linear Plot of CV peak current ($i_{p,a}$) vs square root of scan rate of Complex **1** suggesting homogeneity and it's a substrate diffusion controlled process.

Figure S4. EPR spectra of Complex **1** in (A) organic medium (DMF) (B) pH 7 and pH 10.50 buffer. EPR spectra was recorded at 10 K using X-band continuous wave Bruker EMX PLUS spectrometer (BrukerBioSpin, Rheinstetten, Germany) equipped with standard resonator for high sensitivity CW-EPR operating with a microwave frequency of 9.386632 GHz, microwave power 0.6325 mW, modulation amplitude of 0.5 mT and sweep time 60 s. The spectrum was collected over multiple runs. Modulation frequency was 100 kHz.

Figure S5. (A) Cyclic Voltammetry diagrams of 0.5 mM complex **1** using glassy carbon working as well as counter electrode and Ag/AgCl/1M KCl reference electrode at variable scan rate ranging from 20 mV/s to 300 mV/s in 0.1 M pH 7 phosphate buffer; (B) The plot of i_d vs square root of scan rate ($v^{1/2}$) at pH 7, suggesting no decomposition or deposition onto the electrode surface.

Figure S6. The plot of i_{cat}/i_d vs $1/(v^{1/2})$ from which TOF is calculated at pH 10.5.

Figure S7. Absorption spectra of 0.75 mM complex **1** before (green line) and after 20 min of BE (red line) in pH 7 buffer. For pH 10.50 buffer, blue line and sky blue line in absorption spectra represent before and after 45 min of BE, respectively, of the electrolytic solution on the graphite rod electrode as a working electrode.