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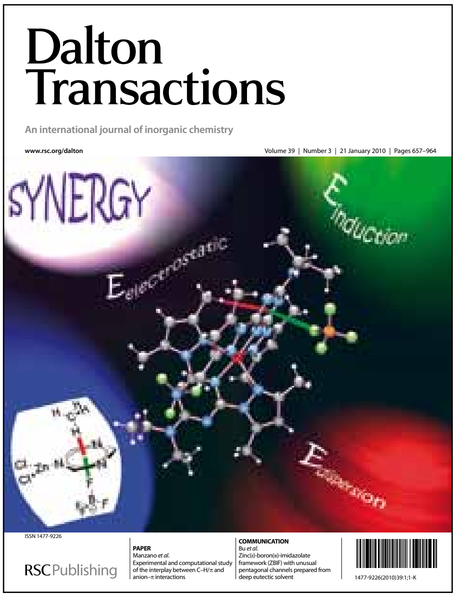

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The first example of centro-symmetrical bis(imido)-bridged dinuclear cobalt(III) complex: synthesis via oxidative dehydrogenation and phenoxazinone synthase activity†

Anangamohan Panja *[,a,b,c] **and Philippe Guionneau** [a,b]

[a] *CNRS, ICMCB, Groupe des Sciences Moléculaires, UPR 9048, F-33608 Pessac, France*

[b] *Université de Bordeaux, ICMCB, UPR 9048, Pessac, F-33600, France*

[c] *Postgraduate Department of Chemistry, Panskura Banamali College, Panskura RS, Purba Medinipur, West Bengal 721152, India*

Corresponding Author

E-mail: ampanja@yahoo.co.in

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ABSTRACT

A bis(imido)-bridged dinuclear cobalt(III) complex, $[Co_2(amp)_2(\mu\text{-imp})_2Cl_2]Cl_2\cdot 2H_2O$ (**1**) [amp = 2-aminomethylpyridine; imp = 2-iminomethylpyridine anion], was synthesized by the reaction of cobalt(II) chloride with 2-aminomethylpyridine in the presence of alkaline hydrogen peroxide at room temperature. X-ray crystallography reveals that both the metal centres in the molecule are related to each other through an inversion centre, and the geometry of each of the Co^{III} ion is a distorted octahedral structure having a CoN_5Cl coordination environment. The most important feature of the structure is the modification of half of the coordinated amines by the oxidative dehydrogenation process which involve in doubly bridging in the complex cation. To the best of our knowledge, this is the first example of bis(imido)-bridged dinuclear cobalt(III) complex derived from metal-assisted oxidative

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dehydrogenation of the coordinated primary amine ligand. Complex **1** was found to be an excellent functional model for the phenoxazinone synthase, catalyzing the oxidative coupling of 2-aminophenol to the corresponding 2-aminophenoxazinone chromophore in dioxygen saturated methanol. The detailed kinetic investigations reveal that the phenoxazinone chromophore is produced via a potential complex-substrate intermediate.

Introduction

Imines are useful intermediates in the synthesis of biologically active nitrogen-containing organic compounds and pharmaceutical substances, thus the transition metal-promoted oxidation of amines has attracted extensive attention.[1,2] Substantial progress has been made in recent years in the development of oxidation reactions for the synthesis of imines from secondary amines; notable examples include stoichiometric oxidation with *N*-*tert*-butylphenylsulfinimidoyl chloride[3] or 2-iodoxybenzoic acid (IBX),[4] metal-catalyzed oxidation with H_2O_2, ^{t}BuOOH, PhIO, or $K_2S_2O_8$,[5] iridium-catalyzed dehydrogenation,[6] along with osmium, ruthenium, cobalt, copper, and iron catalyzed aerobic oxidation.[7-11] However, comparatively little attention has been committed to the oxidation of primary amines, probably because the corresponding imines usually constitute intermediate products that are rapidly dehydrogenated to nitriles due to the reactivity of the second α-amino hydrogen.[12] Although the oxidative dehydrogenation of amines by the assistance of coordinated metal centres involving a variety of mono-, bi- and multidentate ligands, has been described, the reports on crystal structures of the concerning imine coordinated metal complexes are scarce.[10,11,13] Therefore, it remains a challenge to structurally characterize of the imine-coordinated metal complexes that are expected to disclose some relevant informations for the further development of metal-assisted dehydrogenation of coordinated amines.

The design of dinuclear metal complexes incorporating suitable bridging ligands has

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attracted considerable research interest in recent years,[14,15] primarily due to their relevance for biological processes, molecular electronics and for theoretical studies of electron transfer processes.[16-18] As far as biochemistry is concerned, the enzyme phenoxazinone synthase,[19,20] a multicopper oxidase is found naturally in the bacterium *Streptomyces antibioticus* and catalyzes the oxidative coupling of two molecules of a substituted 2-aminophenol to the phenoxazinone chromophore in the final step for the biosynthesis of actinomycin D.[21] This is used clinically for the treatment of Wilm's tumour, gestational choriocarcinoma, and other tumors.[22,23] The synthesis and investigation of functional model complexes for metalloenzymes that mimic the oxidase (oxygenase) activity is therefore of great importance in the development of new and efficient catalysts for oxidation reactions. Only a few functional models based on cobalt have been reported which show phenoxazinone synthase activities.[24]

We have recently reported the study of the catechol oxidase/dioxygenase activity of mononuclear Cu(II) and iron(III) complexes and also stoichiometric oxidation of 2-aminophenol by a mononuclear cobalt(III) complex.[25,26] The catalytic inefficiency of the reported cobalt(III) complex is mainly due to failure of regeneration of the catalyst during course of the reaction.[26] In order to explore better functional models for the phenoxazinone synthase, herein, we report the synthesis, physiochemical and spectral properties of the first structurally characterized bis(imido)-bridged dinuclear cobalt(III) complex, $[Co_2(amp)_2(\mu\text{-imp})_2Cl_2]Cl_2\cdot 2H_2O$ (**1**) [amp = 2-aminomethylpyridine; imp = 2-iminomethylpyridine anion], derived from the oxidative dehydrogenation of half of the coordinated amine ligand at mild condition (Scheme 1). The synthesized dinuclear complex shows phenoxazinone synthase-like activity, and the detailed kinetic investigations concerning this activity are described.

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Experimental section

Materials and physical measurements

Chemicals such as 2-aminomethylpyridine, 2-aminophenol and cobalt(II) chloride hexahydrate were purchased from Aldrich and Alfa Aesar. All other chemicals and solvents were of reagent or analytical grade and were used without further purification.

Elemental analyses for C, H, and N were performed in a Thermo Fischer Flash EA1112 analyzer. The infrared spectra of the sample in KBr disk was 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, glassy-carbon electrode, and Ag/AgCl reference electrode. UV-vis spectra of the complex were measured using a PerkinElmer Lamda-35 spectrophotometer with a 1 cm path-length quartz-cell. Electrospray ionization mass (ESI-MS positive) spectra were recorded on a MICROMASS Q-TOF mass spectrometer.

Synthesis of $[Co_2(amp)_2(\mu\text{-}imp)_2Cl_2]Cl_2\cdot 2H_2O$ (1)

A mixture of $CoCl_2\cdot 6H_2O$ (238 mg, 1.0 mmol) and 2-aminomethylpyridine (216 mg, 2.0 mmol) was mixed together in 40 mL of methanol. The resulting red solution was treated with a mixture of H_2O_2 and NaOH (4.0 mmol) in 1 mL of water with stirring for 10 min at room temperature, during which time the mixture was turned brownish-red. The brown mass of complex **1** was isolated by evaporation of solvent under reduced pressure. Recrystallization from methanol afforded crops of brownish-red blocks of the complex and were isolated via suction filtration, washed with diethyl ether, and air dried. Yield: 151 mg (42%). Anal Calcd. for $C_{24}H_{30}Cl_4Co_2N_8O_2$: C, 39.91 %; H, 4.19 %; N, 15.51%. Found: C, 40.08 %; H, 4.22 %; N, 15.36 %. IR (KBr, cm^{-1}): 3448 (br; $\nu_{O\text{-}H}$); 3204 (w; $\nu_{N\text{-}H}$); 3112-2972 (w; $\nu_{C\text{-}H}$); 1643 (s; $\nu_{C=N}$).

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X-ray crystallography

Suitable single crystal of complex **1** was coated with N-paratone oil, picked up with a nylon fibre and mounted in the cold nitrogen stream operating at 250 K of a Nonius Kappa CCD diffractometer equipped with a Mo-target rotating anode X-ray source and a graphite monochromator (Mo-Kα, λ = 0.71073 Å). Cell refinement, indexing, and scaling of the data set were performed using the programs DENZO-SMN and SCALEPACK.[27] The structures were solved by direct methods and subsequent Fourier analyses, and refined by the full-matrix least-squares technique based on F^2 with the SHELXL97 program using all the reflections.[28] All the non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms belonging to the complex were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. All the calculations were performed using the WinGX System, Ver. 1.70.01.[29] Crystal data and details of data collection and refinement for complex **1** are summarized in Table 1. CCDC 883590 contains the supplementary crystallographic data for complex **1**.

Kinetics of the oxidation of 2-aminophenol

The phenoxazinone synthase activity of the dinuclear cobalt(III) complex was studied by the reaction with 2-aminophenol at 25 ºC in methanol by the UV-vis spectroscopy. Kinetics of the aerobic oxidation of 2-aminophenol catalyzed by complex **1** was measured monitoring change in the absorbance as a function of time at 433 nm ($\varepsilon = 24 \times 10^3$ M^{-1} cm^{-1}), which is characteristic of 2-aminophenoxazin-3-one in methanol. In a first test series, varying amounts of the catalyst, $(5 - 100) \times 10^{-5}$ M, were added to a fixed concentration (1×10^{-2} M) of substrate in methanol (2.0 mL) saturated with dioxygen. In a second test series, 5×10^{-5} M solution of the complex was mixed with varying concentrations of substrate (0.5 – 20) mM in dioxygen saturated methanol (2.0 mL). The initial rate method was applied to determine the

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rate of a reaction, and the average initial rate over three independent measurements was determined by linear regression from the slope of absorbance versus time plot.

Results and discussion

Synthesis and general characterizations

Reaction of 2-aminomethylpyridine (amp) with cobalt(II) salt generally yields bis(amp) or tris(amp) chelated cobalt(III) complexes by the oxidation of molecular dioxygen.[30] It is well established that peroxo-bridged dinuclear cobalt(III) complexes having various nitrogen donor ligands are usually formed in aerobic condition which thereafter produces imine functionalities of the coordinated amines in basic media by the degradation of the peroxo-intermediate.[31,32] In most of cases, an elevated temperature was employed in order to facilitate such oxidative dehydrogenation of amines. Based on this view, we intended to produce an imine functionality by the reaction of 2-aminomethylpyridine with cobalt(II) chloride in alkaline media. The spectra of the resulting blue solution is consistent with the cobalt(II) species[33] (Fig. S1†) and on standing at least for half an hour no significant spectral modification was noticed. Thus, at the present reaction condition either the reactive cobalt-dioxygen species was not formed or it was relatively weak to assist the oxidative dehydrogenation of the coordinated primary amine. However, peroxo-adducts of cobalt(III) may be produced by the direct treatment of hydrogen peroxide with cobalt(II) complex in the presence of a base at low temperature.[34] It is also reported that an additional oxidant, such as hydrogen peroxide, is required in some systems to start the reaction and different imines were produced as a result of the oxidative dehydrogenation reactions. Based on the above observations, we envisioned that alkaline hydrogen peroxide may produce peroxo-adduct of cobalt(III) complex coordinated to 2-aminomethylpyridine at room temperature, which may rapidly generate radical species that be responsible for the oxidative dehydrogenation of coordinated amine. Accordingly, the present bis(imido)-bridged dinuclear cobalt(III) complex

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was synthesized by the reaction of cobalt(II) chloride with 2-aminomethylpyridine in 1:2 molar ratio in methanol, followed by treatment with alkaline H_2O_2 in aqueous medium at room temperature (Scheme 1). Brownish-red crystals of complex **1** were isolated by the slow evaporation of methanol solution in moderate yield. The use of strong alkaline base helps to deprotonate the resulting imine and to produce the bis(imido)-bridged dinuclear complex. The complex was characterized by the elemental analysis, and various spectroscopic and physiochemical methods. The infrared spectral data of the complex are reported in the Experimental Section with tentative assignments. The IR spectrum of the complex shows a broad band observed at 3448 cm^{-1} assigned to solvent water molecules that illustrate the involvement of strong hydrogen bonding by water molecules in the crystal packing. The most significant feature of IR spectra is the presence of a band at 1643 cm^{-1}, attributed to $\nu_{C=N}$ for imine functionalities, which is in good agreement with the X-ray crystal structure of the complex (*vide infra*).

Description of the crystal structure of complex 1

The molecular structure of the dinuclear cobalt(III) complex was determined by single crystal X-ray diffraction technique. Crystallographic data and the details of data collection and refinement for the complex are assembled in Table 1. The important bond lengths and angles are summarized in Table 2. The compound crystallizes in the triclinic $P\bar{1}$ space group, where the asymmetric unit corresponds to half of the molecule. The perspective view of complex cation of **1** along with the selected atom numbering scheme is depicted in Fig. 1. The complex cation is formed by a bis(imido)-bridged Co^{III} dimer, and in the molecular structure two metal centres are related to each other through an inversion centre which bisects Co1 and Co1a and also N4 and N4a. A C_2 rotation about this point of origin transposes the coordinates of half of the atoms in the molecule to their ‘a’ equivalents. The geometry of each of the Co^{III} ion can be best described as a distorted octahedral structure; the CoN_5Cl

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coordination environment is comprised of two imido-bridged nitrogen atoms, one amine nitrogen atom, two pyridyl nitrogen atoms, and one chloride ion. Importantly, the imino ligand lies on the same plane along with the Co^{III} centre as expected from their electronic structure, and the maximum deviation from the mean plane defined by N4–C1–C2–C3–C4–C5–N3 observed for N3 is 0.012 Å. The C–N$_{imino}$ bond distance of 1.263(5) Å, is significantly shorter than the C–N$_{amine}$ bond (1.478(5) Å) as expected.[35] The Co–N$_{amine}$, average Co–N$_{imino}$, mean Co–N$_{pyridine}$, and Co–Cl bond lengths are 1.947(3), 1.895(3), 1.965(3) and 2.264(1), respectively, which are in good agreement to those found in the related cobalt(III) complexes.[30,36] The Co–N$_{imino}$ bond length is shorter than Co–N$_{amine}$, indicating that the deprotonated bridging imino-N coordinates more strongly to the metal centre than the primary amine group. Average bite angel of the bidentate ligands, 82.54(14)º, deviates significantly from 90°, which is the main reason for the structural distortion of complex **1** from the ideal geometry. The intramolecular separation between the two imido-bridged Co^{III} centres is 2.925(1) Å, which is comparable to the metal-metal separations found in many multinuclear metalloenzymes showing oxidase activity.[37] The molecular packing of the complex is stabilized by several π···π stacking interactions between the aromatic rings (Fig. S2†), and the moderately strong hydrogen-bonding interactions involving primary amines, solvent water molecules and Cl^{-} ions (Table 3).

Co^{III} ions in mononuclear complexes with 2-aminomethylpyridine have been reported to be six-coordinate with octahedral geometry in which the coordinated nitrogen atoms of primary amine was not oxidatively dehydrogenated.[30] In the present complex, the main feature of the structure is the modification of the coordinated ligand: the C1–N4 distance [1.263(5) Å] indicates the presence of an imine moiety, which is consistent with the spectroscopic studies (*cf.* below). The structure of complex **1** can only be compared with an imidomalonato-bridged binuclear Co^{III} complex which was synthesized by the reaction of

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$[CoCl_2(tren)Cl.H_2O$ [tren = tris(2-aminoethyl)amine] with α-aminomalonate anion in the presence of triethylamine at elevated temperature. In the crystal structure, an imido-bridge is stabilized by the simultaneous coordination of malonato groups to the metal centres.[35] But in the present structure, the complex is simply stabilized by the two imido-bridges, and this remarkable stability arises mainly from the strong Co–N_{imino} bonding, indicative of the significant cooperation of two imido-bridges in the molecule. To the best of our knowledge, complex **1** is the first example of a doubly imido-bridged cobalt(III) complex.

Dehydrogenation of coordinated 2-aminomethylpyridine

Dehydrogenation of the coordinated amine ligand was further established by UV-vis and IR spectroscopic methods. For this purpose, shortly after mixing of cobalt(II) chloride and 2-aminomethylpyridine, the UV-vis spectrum of a methanol solution was recorded. It displays an absorption maxima at 252 nm ($\varepsilon = 5.6 \times 10^4$) and a shoulder at 368 nm. Upon addition of an aqueous solution of alkaline hydrogen peroxide, a vigorous reaction had been observed and ultimately resulted in a dark brown solution. The UV-vis spectroscopy reveals that two new absorption bands at 344 nm ($\varepsilon = 1.2 \times 10^4$) and 541 nm ($\varepsilon = 2.4 \times 10^3$) with isobestic points observed at 282, 381 and 497 nm, clearly supporting the formation of a new product [Fig. 2]. The band at 541 nm can be assigned to the deprotonated imine to metal charge transfer; the facile charge transfer, consistent with the crystal structure of the dinuclear complex where imine nitrogen atoms are firmly bound to the metal centres. In order to get further insight into the solution species, the mass spectroscopy (ESI, positive mode) of the resulting solution was carried out. The base peak at m/z = 307.0298 observed in the mass spectra can be assigned to monocationic half-molecule of complex **1**, $[Co(amp)(imp)Cl]^+$, confirmed by the isotopic distribution patterns (Fig. S3†). In addition, a weak peak observed at m/z = 613.1391 corresponds to the monocation of dimer, [**1**–H]$^+$, consistent with the isotopic distribution patterns. The mass spectroscopic results unambiguously suggest that the major species produced by the oxidative dehydrogenation of coordinated 2-aminomethylpyridine in solution is **1**.

The Infrared spectroscopy is also a good tool for monitoring the conversion of dehydrogenation of an amine. IR spectrum of a mixture of cobalt(II) chloride and 2-aminomethylpyridine in 1:2 molar ratio in methanol shows a band at 1613 cm^{-1} that might be due to the C=N stretching of pyridyl moieties [Fig. S4†]. Upon addition of the alkaline hydrogen peroxide the peak was shifted to higher frequency with band maximum at 1640 cm^{-1} which clearly indicates the conversion of a primary amine to an imine via an oxidative dehydrogenation process. The ease of oxidative dehydrogenation of the coordinated 2-aminomethylpyridine is probably due to the conjugated structure of the resulting imine, which is consistent with crystal structure of complex **1**. The spectroscopic results, together with the crystal structure of the complex clearly demonstrate the oxidative dehydrogenation of the coordinated primary amine to imine functionality - the metal ion associated with hydrogen peroxide in basic media plays a significant role in this oxidative dehydrogenation process. The presence of an alkali metal cation is strong enough to deprotonate the imine group of coordinated ligands, resulting in a formation of the imido-bridged dinuclear cobalt(III) complex.

Most of the previous reports on metal ion promoted dehydrogenation of the coordinated amines by cobalt complexes describe that the key intermediate for the oxidation of amines is the peroxo-adduct of the cobalt(III) complex.[31,32,38-41] In the presence of a base, cobalt(II) species activates molecular dioxygen for the catalytic dehydrogenation of the coordinated amine groups. The elevated temperature was used in most cases to facilitate the dehydrogenation process. However, similar intermediate may be generated by the treatment of a coordinatvely unsaturated cobalt complex with hydrogen peroxide in basic medium at low temperature.[34] UV-vis spectral data suggest that molecular dioxygen is unable to start

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oxidative dehydrogenation of the coordinated primary amine, and an external activator, such as hydrogen peroxide, is required for this chemical transformation (Fig. S1†). As with all the reported cobalt complexes which show oxidative dehydrogenation of amines,[31,32,38-41] in the present study, the peroxo-adduct rapidly decomposes and subsequently produces bis(imido)-bridged dinuclear cobalt(III) complex **1**.

Electrochemical studies

The function of a redox active metalloenzyme is to catalyze a redox process; therefore, study of the electrochemical properties of their models is of profound importance especially at identical experimental conditions of the kinetic studies. The electrochemical data of the complex has been recorded in methanol containing 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte at a glassy-carbon working electrode and using a Ag/AgCl reference electrode. Cyclic voltammogram of complex **1** shows an electrochemically irreversible peak at –0.70 V both in aerobic and inert conditions which is assigned to the reduction of the cobalt(III) centres to cobalt(II) (Fig. 3). The irreversible nature of the electrochemical process may be due to the instability of Co^{II} species on the electrode surface presumably by the loss of a labile chloride ion from the coordination sphere. Moreover, the Co^{II} species is formed at a quite negative potential which indicates that complex **1** may not be a suitable catalyst for oxidation reactions although the regeneration of catalyst is quite favourable in aerobic condition. An irreversible oxidation response at 0.54 V attributed to the oxidation of 2-aminophenol under identical conditions supports this fact (Fig. S5†). But the electrochemical scenario of the reactants may be dramatically changed if a catalyst-substrate adduct is formed during the course of a redox transformation, and in such a situation facile oxidation of the coordinated 2-aminophenol by Co^{III} centre through an inner-sphere electron transfer pathway would be possible. In fact, the rate saturation kinetic profile (*cf.* below) strongly suggests the formation of complex-substrate adduct prior to the electron transfer

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process.

Phenoxazinone synthase activity and kinetic studies

The catalytic activity of complex **1** for the oxidation of 2-aminophenol (OAPH) by molecular O_2 was evaluated spectrophotometrically in dioxygen-saturated methanol at 25 ºC. The reactivity studies were performed in methanol because of good solubility of the complex, substrate and as well as their product. In order to avoid the autoxidation of the substrate by air the catalytic activity was checked in absence of added base. Before proceeding into the detailed kinetic study, it is necessary to check the ability of the complex to oxidize 2-aminophenol. For this purpose, 5×10^{-5} M solution of complex **1** was treated with 100 equivalents of OAPH under the aerobic condition. The course of the reaction was followed by UV-vis spectroscopy by monitoring increase in the absorbance at 433 nm, corresponding to the formation of the phenoxazinone chromophore. Time dependent spectral change for the period of 2 h after the addition of OAPH to the methanolic solution of the complex is depicted in Fig. 4. The spectral scan reveals the increase of peak intensity at 433 nm characteristic for phenoxazinone chromophore formed over time. The product was isolated after 24 h of reaction, and analyzed by GC, which showed the formation of 2-aminophenoxazine-3-one as the sole product with 100% conversion.

The reaction kinetics of the oxidation of OAPH was determined by the method of initial rates by monitoring the growth of 433 nm band of the product 2-aminophenoxazine-3-one. The concentration of the substrate OAPH was always kept at least 10 times higher than that of the complex to maintain the pseudo-first-order condition. All the kinetic experiments were carried out at constant temperature of 25 ºC, monitored with a thermostat. In order to explore the dependence of the rate on the substrate concentration, a fixed concentration of complex **1** (5×10^{-5} M) was treated with varying concentrations of the substrate from 5×10^{-4} M to 1×10^{-2} M, and the formation of 2-aminophenoxazine-3-one was monitored over time at 433 nm.

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Initial rates were determined by linear regression from the slope of the absorbance versus time plot for each concentration of the substrate and each experiment was repeated three times with a variation of ± 4%. The average rate of the reactions show that the rate is first order at the region of low concentrations of the substrate OAPH while zero order at its higher concentrations (Fig. 5). This observation indicates that the oxidation of OAPH proceeds through the formation of a relatively stable intermediate, complex-substrate adduct, presumably formed by the coordination of substrate to catalyst by the replacement of a chloride ion, followed by the irreversible substrate oxidation in the rate-determining step of the catalytic cycle. This type of saturation rate dependency on the concentration of the substrate may be explained by considering Michaelis-Menten model, originally developed for the enzyme kinetics. Analysis of the experimental data yielded an equilibrium constant (K_M) value of 1. 57 × 10^{-3} and V_{max} value of 1.91 × 10^{-7} M^{-1} s^{-1}; these are also verified by the Lineweaver–Burk plot. The k_{cat} value is obtained by dividing the V_{max} by the concentration of the complex used, and is found to be 3.82 × 10^{-3} s^{-1}. Although the turnover rate of 13.75 h^{-1} is moderate enough, reactivity of which cannot be compared to the reported functional models of phenoxazinone synthase as most of the cases turnover numbers are not evaluated.[42,43] Moreover, for a particular substrate concentration, varying the complex concentration, a linear relationship for the initial rates was obtained, which shows a first-order dependence on the complex concentration (Fig. S6†). Based on the above results, a possible mechanism OAPH oxidation catalyzed by complex **1** is proposed (Scheme 2). At the first step OAP forms an adduct with the dinuclear cobalt(III) complex, which yields OAP radical in the rate determining step. The OAP radical may generate *o*-benzoquinone monoamine (BQMI) in many ways including the disproportionation of the OAP radical itself. Ultimately, 2-aminophenoxazine-3-one is produced via several oxidative dehydrogenation processes involving OAPH, O_2, and BQMI as shown in Scheme 2.

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Conclusions

A dinuclear cobalt(III) complex was synthesized by the oxidative dehydrogenation of coordinated 2-aminomethylpyridine in the presence of alkaline hydrogen peroxide. The X-ray crystal structure reveals an unprecedented bis(imido)-bridged dinuclear cobalt(III) complex in which both the octahedrally coordinated metal centres are related to each other through an inversion centre. The spectroscopic results suggest that the alkaline hydrogen peroxide plays a significant role in the oxidative dehydrogenation of the amine at mild condition. The complex was found to be an excellent functional model of phenoxazinone synthase, catalyzing the oxidative coupling of 2-aminophenol to the corresponding phenoxazinone chromophore in dioxygen saturated methanol medium via a catalyst-substrate intermediate. Apically coordinated labile chloride ion apparently helps to the formation of a catalyst-substrate intermediate, and thereby, increases the catalytic efficiency of the complex. The metal-metal separation in the molecule of 2.925 Å is comparable to the separations found in many multinuclear metalloenzymes, and thus the present report would encourage the chemists for the synthesis of imido-bridged di- or multi-nuclear complexes for the development of functional models of various metalloenzymes.

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† Electronic supplementary information (ESI) available: The electronic supplementary information file contains Figs. S1–S6. CCDC 883590 contains the supplementary crystallographic data for complex **1**. For ESI and crystallographic data in CIF or other electronic format see DOI:

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Table 1. Crystal data and structure refinement of dinuclear complex **1**

Empirical formula	$C_{24}H_{30}Cl_4Co_2N_8O_2$
Formula weight	722.22
Temperature (K)	250(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.5370(10)
b (Å)	8.9420(10)
c (Å)	10.680(2)
α (º)	70.914(6)
β(°)	75.052(6)
γ (º)	75.559(7)
Volume (Å^3)	732.14(18)
Z	2
D_{calc} (g cm^{-3})	1.638
Absorption coefficient (mm^{-1})	1.536
F(000)	368
Crystal size (mm)	0.10 × 0.0 5 × 0.03
θ Range for data collection (°)	4.12 – 26.37
Limiting indices	$-01 \leq h \leq 8$, $-11 \leq k \leq 11$, $-13 \leq l \leq 13$
Reflections collected / unique	4893
Indipendent reflection / R_{int}	2970 / 0.0493
Observed reflections	2046
Completeness to 2θ (%)	99.1
Data / restraints / parameters	2970 / 0/ 181
Goodness-of-fit on *F*2	1.011
Final *R* indices [I>2σ(I)]	R1 = 0.0478, wR2 = 0.1046
R indices (all data)	R1 = 0.0832, wR2 = 0.1187
Largest diff. peak / hole (e Å^{-3})	0.937/–0.436

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Table 2. Selected bond lengths (Å) and bond angles (º) for **1**

Co1 – N1	1.981(3)	Co1 – N4	1.884(3)
Co1 – N2	1.947(3)	Co1 – N4#	1.907(3)
Co1 – N3	1.950(3)	Co1 – Cl1	2.2645(11)
Co1 – Co1#	2.9255(11)		
N4 – Co1 – N1	173.84(13)	N2 – Co1 – N3	91.04(14)
N4 – Co1 – N1#	96.72(13)	N4 – Co1 – N4#	79.00(14)
N2 – Co1 – N1	82.10(14)	N4 – Co1 – Cl1	90.97(10)
N3 – Co1 – N1	100.25(14)	N4 – Co1 – Cl1#	92.37(10)
N4 – Co1 – N2	93.40(13)	N2 – Co1 – Cl1	175.38(10)
N4 – Co1 – N2#	89.93(13)	N3 – Co1 – Cl1	87.93(10)
N4 – Co1 – N3	83.98(14)	N1 – Co1 – Cl1	93.64(10)
N4 – Co1 – N3#	162.98(14)	Cl1 – Co1 – Co1#	92.17(4)

Symmetry Code: # = 1–x, –y, 1–z

Table 3. Important hydrogen bonds (Å, º) for dinuclear complex **1**

D–H···A	D–H	H···A	D···A	<D–H···A
N2–H2B···Cl2#	0.91	2.302(2)	3.166(4)	158.3(2)
O2–H2O···Cl2	1.00	2.239(2)	3.234(5)	173.7(3)
O2–H1O···Cl2#	0.94	2.295(2)	3.219(5)	167.4(3)

Symmetry Code: # = 1–x, –y, 1–z

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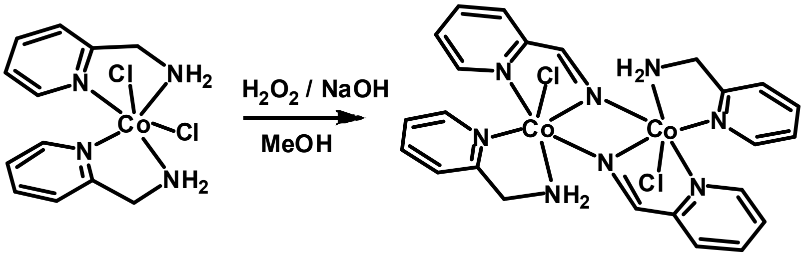
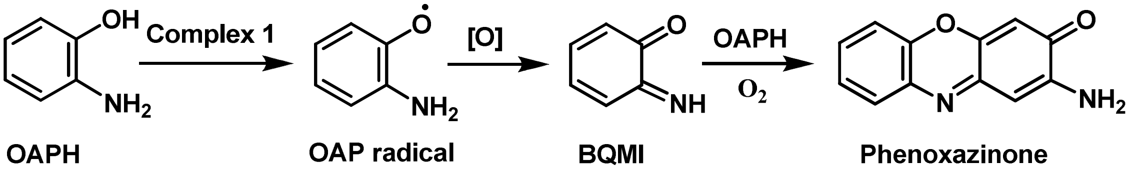


Complex 1

Scheme 1. Schematic representation of synthesis of the dinuclear complex



Scheme 2. Probable mechanism for the formation of phenoxazinone chromophore

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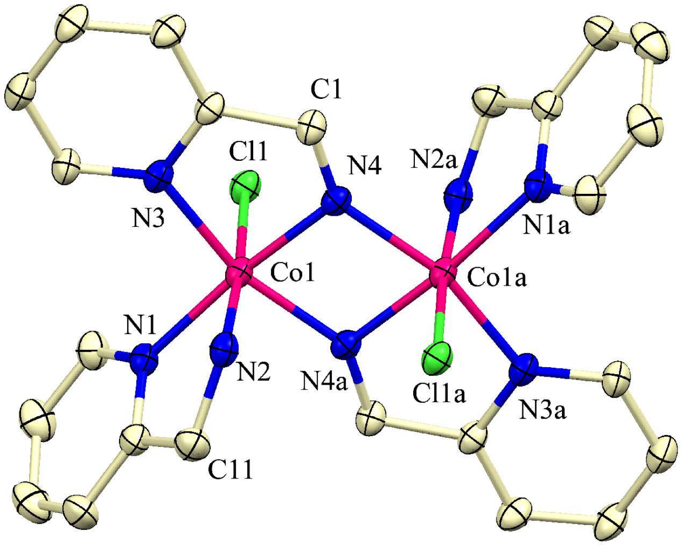

Figure 1: ORTEP diagram of complex cation **1** showing the atom numbering scheme, ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. Symmetry Code: a = 1–x, –y, 1–z

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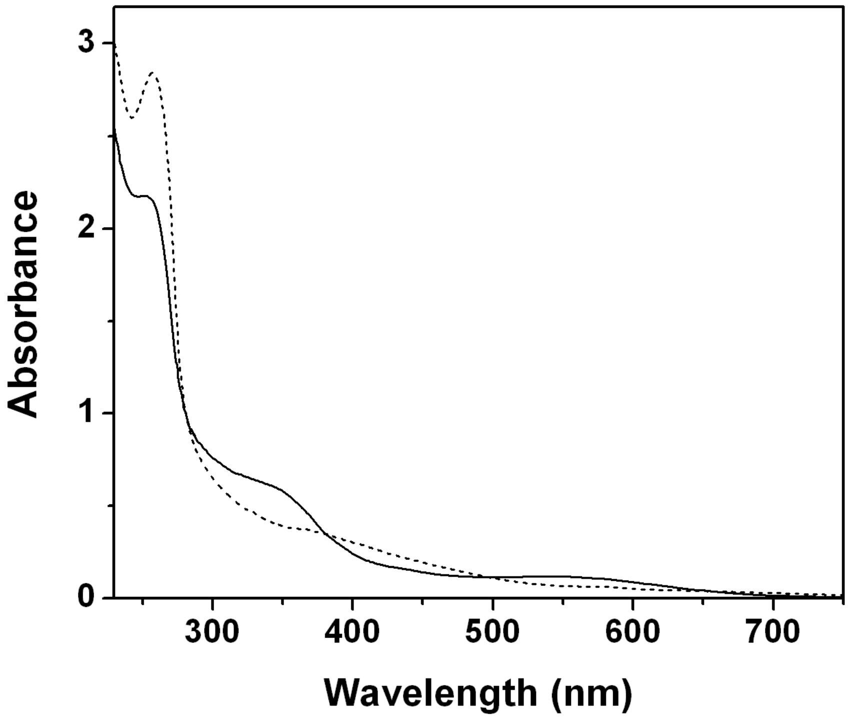

Figure 2. UV-vis spectra of cobalt(II) chloride with 2-aminomethylpyridine in 1: 2 molar ratio in methanol (dashed line) and upon addition of alkaline hydrogen peroxide (solid line).

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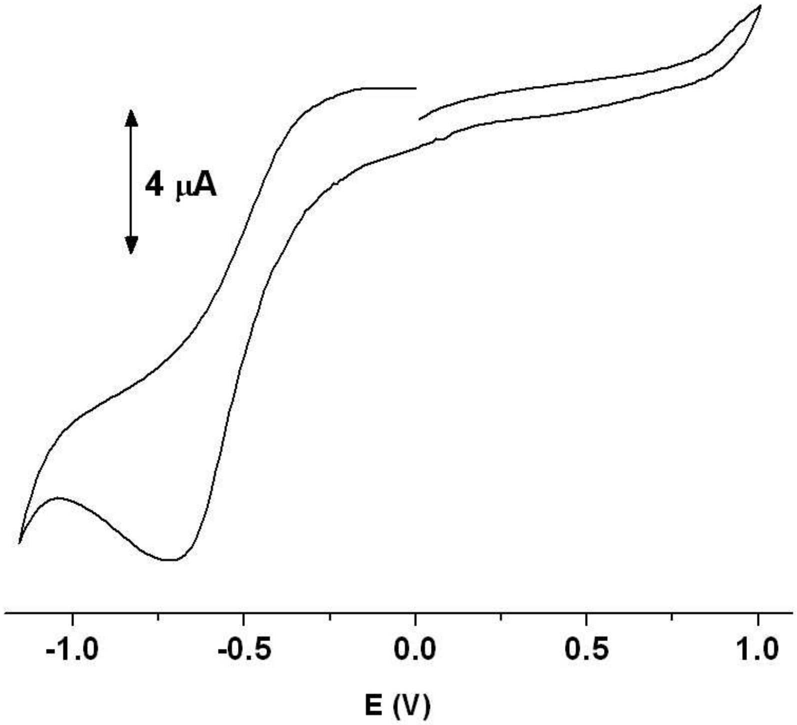

Figure 3. Cyclic voltammogram of the complex in methanol containing TBAP as supporting electrolyte at a scan rate of 100 mV/s.

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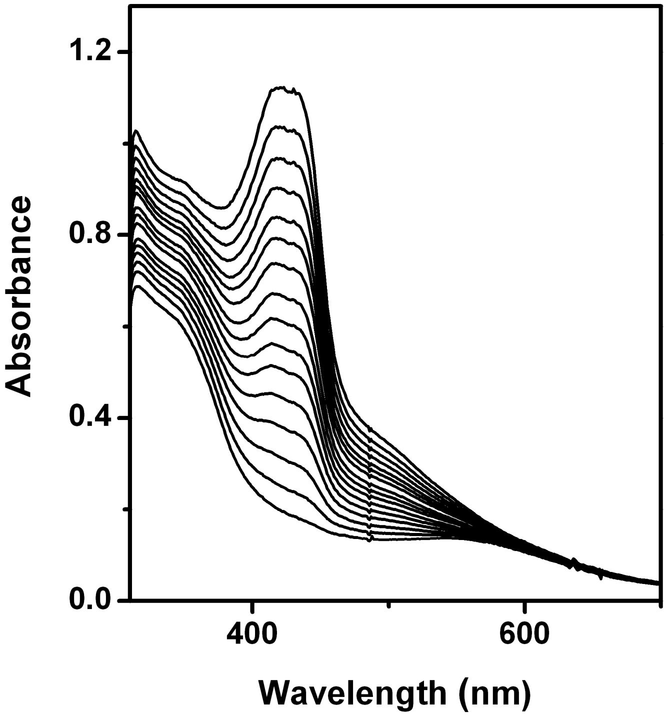

Figure 4. Time resolved UV-vis spectral changes for the oxidation of 2-aminophenol (5 × 10^{-3} mol dm^{-3}) catalyzed by the complex (5 × 10^{-5} mol dm^{-3}) up to 2 h of reaction in dioxygen-saturated methanol at 25 ºC.

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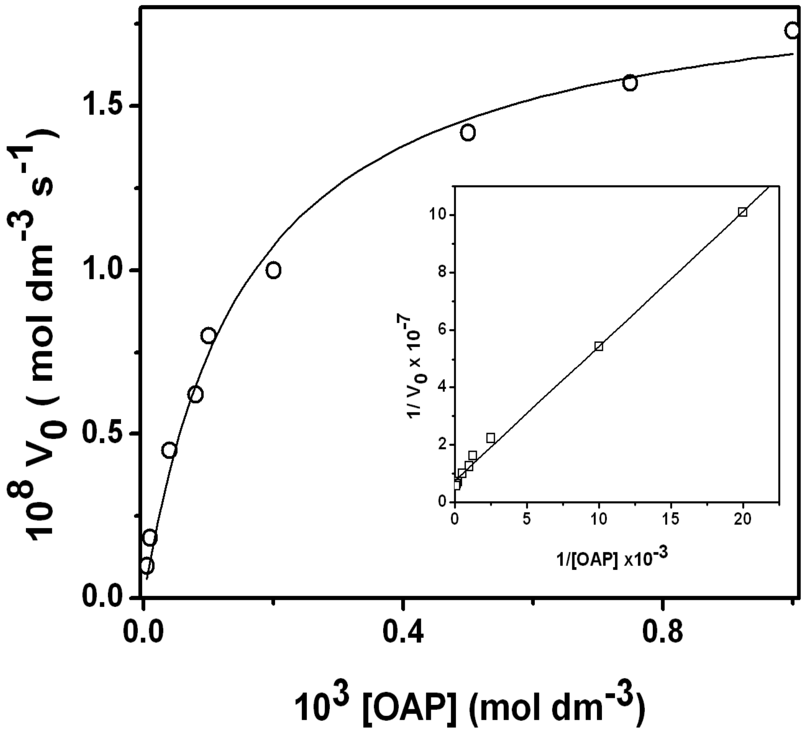

Figure 5. Plot of the initial rates on the OAPH concentrations for the oxidation reaction catalyzed by the complex at fixed concentration in dioxygen-saturated methanol at 25 ºC. Inset shows the reciprocal Lineweaver-Burk plot.

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Graphical Abstract

The first example of centro-symmetrical bis(imido)-bridged dinuclear cobalt(III) complex: synthesis via oxidative dehydrogenation and phenoxazinone synthase activity

Anangamohan Panja and Philippe Guionneau

An unprecedented bis(imido)-bridged dinuclear Cobalt(III) complex derived from the oxidative dehydrogenation of the coordinated primary amine is reported. The phenoxazinone synthase like activity of the complex is also described.