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Synthesis, crystal structure, redox property and theoretical studies of a pyrrole containing cobalt(III) Schiff base compound

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A new mononuclear cobalt(III) complex with a pentadentate Schiff base ligand derived from the condensation of N-(3-aminopropyl)-propane-1,3-diamine with pyrrole-2-aldehyde has been synthesized and structurally characterized by X-ray crystallography. Structural analysis shows that the geometry of cobalt(III) ion is a distorted octahedron in which triamine part of the pentadentate ligand occupies the meridional positions, while two pyrrole nitrogen atoms are in *cis* disposition. Despite the potentially interesting similarities of pyrrole-based ligands to porphyrin systems, the present complex is inactive towards the oxidation of *o*-aminophenol, while analogous systems with pyridine containing ligands have proven to be efficient functional models for phenoxazinone synthase. Although the electrospray ionization mass spectral study clearly indicates the formation of a complex-substrate aggregate, the inability towards oxidation of *o*-aminophenol by the present complex can be explained electrochemically, where strong electron donating ability of the deprotonated pyrrole moiety reduces the possibility of reduction of cobalt(III) to cobalt(II).

Keywords: Coordination chemistry, Schiff bases, Pyrrole ligands, Cobalt, X-ray crystal structures, Density functional calculations, Cyclic voltammetry, Mass spectroscopy

Schiff base complexes have been extensively studied in the coordination chemistry mainly due to their ease of synthesis, tremendous structural diversities and with the aim of shedding light on various aspects of catalytic activity[1–4], as well as role of the metal ions in biological systems[5,6]. The active sites of many metalloenzymes contain transition metal ions, and the redox-active metal centers play important roles in dioxygen binding and oxidation of a variety of important biological substances because they facilitate the spin-forbidden interaction between dioxygen and organic matter[7–9]. Study of the model complexes of such metalloenzymes is therefore of great importance for the development of small molecule catalysts for specific oxidation reactions of organic substances in the industrial and synthetic processes. Over the years much effort has gone into the investigation of complexes of a wide range of Schiff-base ligands, in particular pyridine containing systems, while very little is known about complexes of pyrrole analogues of such ligands, despite the potentially interesting similarities to porphyrins[10–16].

Our studies on transition metal based complexes for biomimetic oxidation of various organic substances, suggest that labile coordination position along with the electronic environment around the metal center play an important role for such activity[17–22]. We have recently reported some cobalt and manganese complexes with pyridine containing ligands and these complexes are found to be efficient functional models for the phenoxazinone synthase, a multicopper oxidase. This enzyme is found naturally in the bacterium *Streptomyces antibioticus*[23,24] and catalyzes the oxidative coupling of two molecules of a substituted *o*-aminophenol to the phenoxazinone chromophore in the final step for the biosynthesis of actinomycin D[25]. Our continuing interest in the bio-inspired catalytic chemistry thus leads us to explore the transition metal complexes with bio-relevant pyrrole containing multidentate Schiff base ligands. In the present endeavor, we report the synthesis and characterization of a mononuclear cobalt(III) complex, $[Co(L)(MeOH)]ClO_4$ (**1**), where H_2L is a pentadentate ligand derived from Schiff base condensation of N-(3-aminopropyl)-propane-1,3-diamine with pyrrole-2-aldehyde[26,27]. Detailed theoretical and analytical studies have also been performed in order to understand the role of the electronic structure of metal complexes to the oxidase mimicking activity.

Materials and Methods

Chemicals such as N-(3-aminopropyl)-propane-1,3-diamine,pyrrole-2-aldehyde and cobalt(II) perchlorate hexahydrate (Aldrich), and *o*-aminophenol (Merck, India) were of analytical grade and used without further purification. Solvents like methanol, diethyl ether and acetonitrile (Merck, India) were of reagent grade and used as received. Elemental analyses for C, H and N were carried out using a Perkin-Elmer 240 elemental analyser. Infrared spectrum was recorded in the range 400–4000 cm^{-1} on a PerkinElmer Spectrum Two infrared spectrometer in KBr pellet. Absorption spectra were measured using a UV-2450 spectrophotometer (Shimadzu) with a quartz cell of 1 cm path length. Cyclic voltammetric experiments were performed at room temperature in methanol using tetrabutylammonium perchlorate as a supporting electrolyte on a CH Instrument electrochemical workstation (model CHI630E). The conventional three-electrode assembly comprised a platinum working electrode, a platinum wire auxiliary electrode and a Ag/AgCl reference electrode. Electrospray ionization mass (ESI-MS positive) spectra were recorded on a Micromass Q-TOF mass spectrometer.

Synthesis of $[Co(L)(MeOH)]ClO_4$ (1)

A mixture of N-(3-aminopropyl)-propane-1,3-diamine (0.262g, 2.0 mmol) and pyrrole-2-aldehyde (0.380g, 4.0 mmol) in a 30 ml of methanol was heated to reflux for 45 min. To the resulting yellow-orange solution of the Schiff base ligand (H_2L), a methanol solution (20 mL) of $Co(ClO_4)_2{\cdot}6H_2O$ (0.730 g, 2 mmol) was added which resulted in a dark-red solution instantaneously. The reaction mixture was refluxed for a further 30 min and allowed to cool at room temperature. A brown powder which separated out from the solution upon addition of ether, was washed with mother liquor followed by ether and air dried. Yield: 0.590 g (60%). Crops of single crystals suitable for X-ray diffraction were grown on slow diffusion of ether into a methanolic solution of the complex. Anal. (%) for $C_{17}H_{21}ClCoN_5O_5$: Calcd.: C, 43.42; H, 4.47; N, 14.90. Found: C, 43.07; H, 4.49; N, 14.80. IR (KBr, cm^{-1}): 3233 br ($\nu_{NH,\ OH}$); 1581 m ($\nu_{C=N}$) ; 1109 s, 1089 s, 623 s ($\nu_{Cl–O}$). UV–vis, nm (ε, dm^3 mol^{-1} cm^{-1}): 354 (39450), 302 (sh, 31250), 218 (71400).

X-ray crystallography

Single crystal X-ray diffraction data of complex **1** were collected on 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[28]. The structure was solved by the direct methods and refined by means of full matrix least-square technique based on F^2 using SHELX-97 software package[29]. All the non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms attached to carbon atoms were placed in their geometrically idealized positions and were constrained to ride on their parent atoms. The hydrogen atoms connected to nitrogen and oxygen atoms were located on the difference Fourier maps and isotropically treated based on their respective parent atoms. Relevant crystallographic informations for the complex are assembled in Table 1.

All the calculations were performed with density functional theory (DFT) implemented in Gaussian09[30]. All the structures were fully optimized

Table 1—Crystal data and structure refinement of complex **1**

Emp. formula	$C_{17}H_{25}ClCoN_5O_5$
Formula wt	473.80
Temp. (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	Cc
a (Å)	11.3609(4)
b (Å)	12.2478(8)
c (Å)	14.3531(8)
β (°)	90.864(4)
Vol. ($Å^3$)	1996.95(19)
Z	4
D_{calc} ($g\ cm^{-3}$)	1.576
Abs. coeff. (mm^{-1})	1.033
F(000)	984
θ Range for data collection (°)	3.59 – 27.49
Reflect. collected	4161
Ind. reflect. / R_{int}	4156 / 0.0107
Data /restraints /parameters	3857/ 2/ 269
Goodness-of-fit on F^2	1.018
Final *R* indices [I>2σ(I)]	*R*1 = 0.0393, w*R*2 = 0.0964
R indices (all data)	*R*1 = 0.0446, w*R*2 = 0.1006
Largest diff. peak /hole (e $Å^{-3}$)	1.040/ -0.500

with B3LYP hybrid functional and 6-31g(d) + for hydrogen, carbon, nitrogen and oxygen, and LANL2DZ basis set for cobalt.

Results and Discussion

Synthesis and characterization

Condensation of N-(3-aminopropyl)-propane-1,3-diamine with pyrrole-2-aldehyde in 1:2 molar ratio at reflux resulted in a yellow-orange Schiff base ligand H_2L. Treatment of *in situ* prepared ligand with $Co(ClO_4)_2{\cdot}6H_2O$ in aerobic condition afforded $[Co(L)(MeOH)]ClO_4$ in high yield. The elemental analyses are consistent with the proposed molecular formula that shows metal/ligand ratio is 1:1. The complex is stable in air and also moisture insensitive, and soluble in common polar organic solvents, e.g., acetonitrile, methanol and DMF. The IR spectrum of *in situ* generated free ligand exhibits the characteristic bifurcated bands of two imine C=N bonds, which appear at 1644 and 1634 cm^{-1}. Similar characteristic imine C=N stretching frequency is observed at 1581 cm^{-1} in the IR spectrum of **1**. The ν(CN) band is generally shifted to lower frequencies relative to the free ligand, indicating a decrease in the C=N bond order due to the coordination of the imine nitrogen to the metal. IR spectrum of **1** also displays a moderately strong peak at 3233 cm^{-1} that indicates O−H stretching vibration of coordinated methanol molecule. Moreover, the IR spectrum shows a very strong bifurcated absorption band in the range 1089–1109 cm^{-1}, which is unambiguously assigned to the stretching frequency of perchlorate ion. The splitting of ν(Cl–O) band may result from the involvement of hydrogen bonding of ClO_4^- ions in the crystal lattice. The bending mode of vibration for ClO_4^- ion is also observed at 623 cm^{-1}.

X-ray crystal structure and DFT study

The crystal structure of the complex was determined by X-ray diffraction study, and the crystallographic analysis reveals that the complex crystallizes in the monoclinic space group Cc. The crystal structure of the complex cation is depicted in Fig. 1 together with the atom numbering scheme, while important bond lengths and bond angles are given in Table 2. The molecular structure of the complex cation of **1** adopts a distorted octahedral geometry as can be judged by the spread in its *cis* angles 81.85(18)–98.77(18)° and *trans* angles 172.29(18)–178.74(16)°. The cobalt(III) center is connected to five nitrogen donor sites of the pentadentate ligand in which both the imine nitrogen atoms are *trans* to each other with a bond angle of

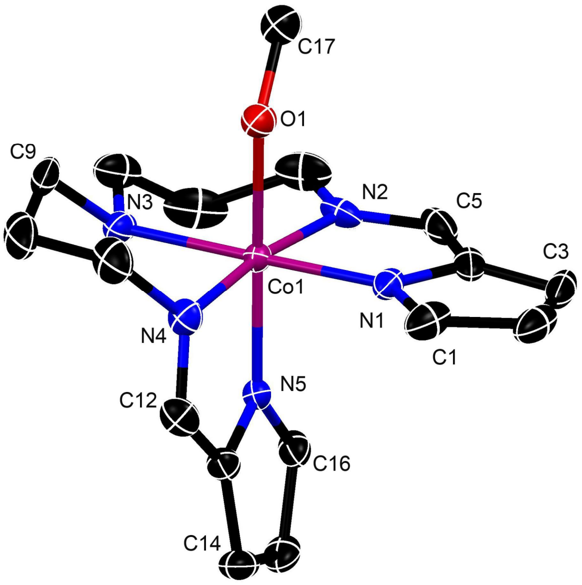


Fig. 1—Molecular structure of **1** showing atom labeling scheme. Ellipsoids are drawn in 30% probability and most of the hydrogen atoms are omitted for clarity.

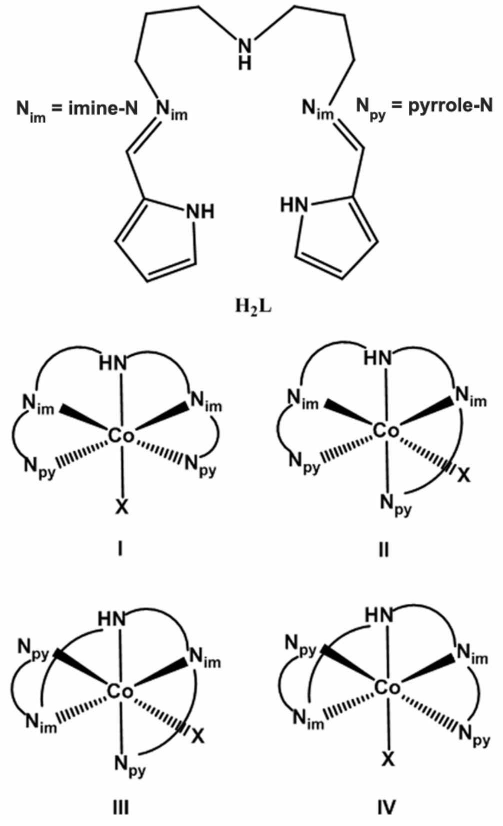
Table 2—Comparison of experimental and calculated crystallographic data

Bond	Bond lengths (Å)		Angle	Bond angles (°)	
	Expt.[a]	Calc.[b]		Expt.[a]	Calc.[b]
Co1–N1	1.910(3)	1.926	N1–Co1–N2	81.85(18)	83.23
Co1–N2	1.925(4)	1.972	N1–Co1–N3	178.74(16)	177.38
Co1–N3	1.994(3)	2.043	N2–Co1–N3	98.77(18)	97.10
Co1–N4	1.934(4)	1.960	N2–Co1–N4	172.29(18)	174.91
Co1–N5	1.889(3)	1.906	N3–Co1–N4	86.83(16)	85.78
Co1–O1	1.975(3)	2.067	N4–Co1–N5	83.03(15)	83.21
C5–N2	1.300(7)	1.313			
C12–N4	1.292(6)	1.315			

[a] X-ray structure of complex **1**; [b] DFT structure of isomer **III**.

172.29(18)° and both the pyrrole nitrogen atoms occupy the *cis* coordination sites with bond angle of 88.09(13)°, and the coordination sphere is completed by methanol binding. The Co–N(imine) [1.925(4) and 1.934(4) Å], Co–N(pyrrole) [1.910(3) and 1.889(3) Å], Co–N(secondary amine) [1.994(3) Å] and Co–O(methanol) [1.975(3) Å] bond lengths are comparable to corresponding distances reported in the literature[15,31,32]. The O1–H1A bond of coordinated methanol molecule forms hydrogen bond with perchlorate oxygen atom (O5) with dimensions O···O 2.810(5) Å, H···O 2.03(6) Å, O–H···O 171°. O2 oxygen atom of the perchlorate ion also forms hydrogen bond with the secondary N–H group (N3–H3A)$^{\#}$ ($^{\#}$ = –1/2+*x*,1/2–*y*,–1/2+*z*) from the neighboring molecule with dimensions N···O 3.033(7) Å, H···O 2.29(7) Å, N–H···O 146°. Eventually, these moderately strong hydrogen bonding interactions lead to the construction of a 1D chain as shown in Fig. 2.

Careful inspection of the crystal structure suggests that the triamine part of the pentadentate ligand occupies the meridional positions, while two pyrrole nitrogen atoms are in *cis* dispositions. Coincidently, conformation of the ligand in **1** is identical to the recently reported cobalt(III) complex with pyridine analogue[21]. However, it is significantly different from the structure of the reported cobalt(III) complex with similar ligand system in which triamine part of the deprotonated ligand occupies three facial sites, while two pyrrole-N atoms are in *cis* positions[31]. These diverse structural characterizations in the solid state prompt us to investigate a computational study using density functional theory (DFT) calculations with B3LYP hybrid functional level. The experimental and calculated structures of isomer **III** are compared in Table 2 through selected geometrical data. The agreement is very good, suggesting that the level of calculation is relevant to study this series of complexes. The DFT calculations on the various isomers (**I**–**IV** in Scheme 1) are in accord with the X-ray structural characterization which suggests that **III** is the most stable isomer (Supplementary Data, Tables S1–S2 and Fig S1). It also shows that meridional conformation of the triamine part of the ligand is more stable than the facial arrangement. Isomer **III** is about 5.59 and 9.97 kcal mol^{-1} lower in energy than that of the isomers **IV** and **II**, respectively, while it is significantly more stable (by 21.57 kcal mol^{-1}) than isomer **I**. In our recent report, the DFT studies suggested that ligand favors the meridional arrangement in the cobalt(III)



Scheme 1

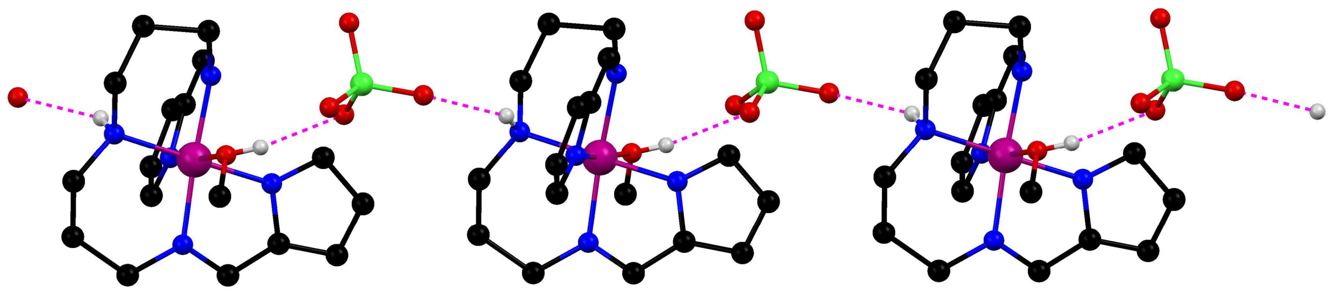


Fig. 2—One dimensional (1D) hydrogen bonded supramolecular chain of **1**. Hydrogen atoms not responsible for hydrogen bonding are omitted for clarity.

coordination chemistry with increasing spacer length[19]. In the present ligand, we have used a triamine with longer propylinic linkers, and both the theoretical and experimental results suggest that the meridional conformation of the ligand is again much more favorable over facial arrangement. Similar compound reported by Meghdadi *et al.*[31] shows that triamine part of the ligand is bonded to the metal center in the facial arrangement in which shorter ethylinic linkers in the triamine part favor this conformation which is along with line of the theoretical studies.

Reaction with *o*-aminophenols

The possibility of phenoxazinone synthase mimicking activity of the complex was studied by monitoring the oxidation of *o*-aminophenol (OAPH) spectrophotometrically in dioxygen-saturated methanol solution at 25 °C. The catalytic studies were performed in the absence of added base to avoid autoxidation of the substrate. In order to examine the ability of the complex to oxidize *o*-aminophenol, a 2.0×10^{-5} *M* solution of the complex was allowed to react with a 0.01 *M* solution of OAPH, and the time resolved spectral scans were recorded up to 2 h in dioxygen saturated methanol at 25 °C as shown in Fig. 3. Catalytically active compounds generally show rapid growth of the peak intensity at *ca*. 433 nm, characteristic of the phenoxazinone chromophore[18–22]. However, the spectral scans reveal no significant growth of the peak intensity at 433 nm, which suggests that the present complex is almost inactive towards the oxidation of OAPH to 2-aminophenoxazine-3-one in aerobic condition. Further studies with substituted *o*-aminophenol suggest that the present complex is unable to oxidize *o*-aminophenol moiety. However, a chemically strong reductant such as L-ascorbic acid is able to reduce the metal center in the present complex.

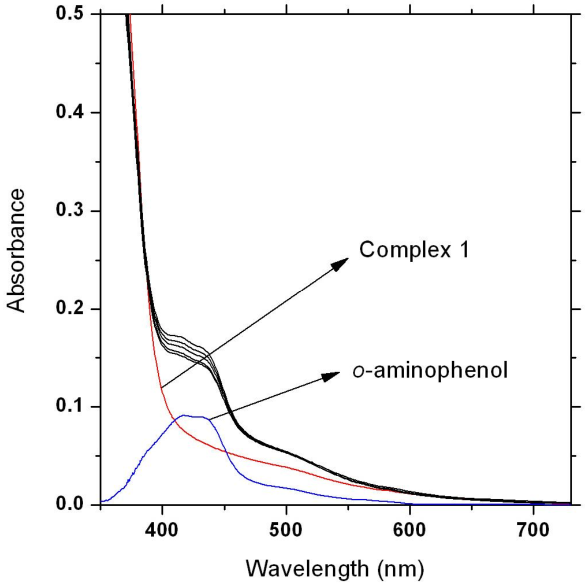


Fig. 3—UV-vis spectral profile for the oxidation of *o*-aminophenol in methanol at 25 °C. [The spectra were recorded for a period of 2 h. [*o*-aminophenol] = 0.01 *M* and [complex **1**] = 2×10^{-5} *M*].

Cyclic voltammetry

The electrochemical potential of the active site of a metalloenzyme plays a central role in catalyzing the oxidation of various organic substances in the living systems. Therefore, it is important to study the electrochemical behavior of their models that provide detailed information about their catalytic ability. The electrochemical data of the complex have been recorded in methanol containing 0.1 *M* tetrabutylammonium perchlorate as a supporting electrolyte in a conventional three-electrode configuration using a Pt disk working electrode, Pt auxiliary electrode, and Ag/AgCl reference electrode. Cyclic voltammetry of **1** in methanol solution at room temperature (Fig. 4) shows a quasi-reversible reduction at $E_{1/2} = -0.78$ V ($E_{pc} = -0.99$ V $E_{pa} = -0.59$ V ΔEp = 0.40 V) that can be attributed to the Co(III)/Co(II) reduction process. In comparison to our previous studies on related complexes with pyridine containing ligands, the present complex is reduced at

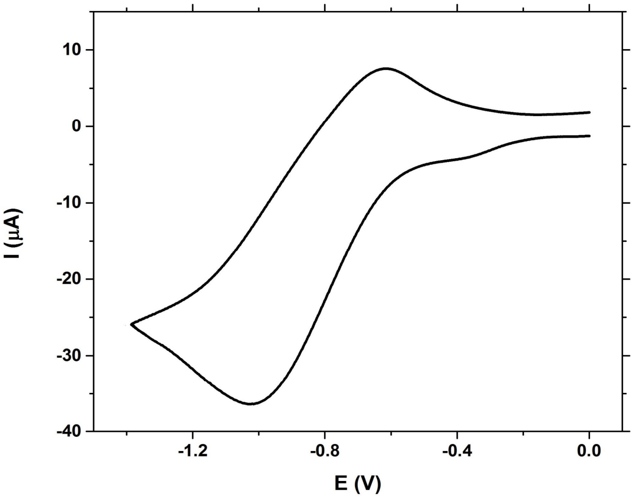


Fig. 4—Cyclic voltammogram of **1** in methanol with a conventional three-electrode system using a Pt working electrode, Pt auxiliary electrode and Ag/AgCl reference electrode in the presence of tetrabutylammonium perchlorate as the supporting electrolyte at ambient temperature. [scan rate: 100 mV s^{-1}].

more negative electrochemical potential[18,21]. This fact can be explained by considering the relative donating ability of the pyridine and pyrrole moieties. The higher electron-donating ability of deprotonated pyrrole moiety than that of neutral pyridine group increases the electron density on the metal center, and thus reduction of cobalt(III) center occurs at more negative electrode potential.

Electrospray ionization mass spectroscopy

The electrospray ionization mass spectrum (ESI-MS positive) of the complex was recorded in methanol solution. In the mass spectrum, the base peak found at *m/z* = 342.11 with line-to-line separation of 1.0 can be assigned to $[Co^{III}(L)]^+$. In order to get an insight into the complex-substrate interaction, ESI-MS positive spectrum of a 1:50 mixture of the complex and *o*-aminophenol in methanol was recorded after 10 minutes of mixing (Supplementary Data, Fig. S2). The mass spectrum of the complex in the presence of excess OAPH shows that it contains the same base peak that is found in the mass spectrum of the complex alone. A new peak at *m/z* = 451.17 with line-to-line separation of unity is quite interesting as it matches with a complex-substrate adduct of formula $[Co^{III}(L)(OAPH)]^+$.

From the structural analysis it is clear that binding of the ligand with metal center is identical to the recently reported cobalt(III) complex with bis(pyridine-imine) analogue[21]. Although these pyridine analogues were active catalysts mimicking the function of phenoxazinone synthase, the present complex was found to be inactive. Thus, the inactivity of complex **1** towards the oxidation of OAPH is, at a first glance, quite surprising as the electrospray ionization mass spectral study clearly indicates the formation of a complex-substrate aggregate. In the previous cobalt(III) based systems[18,21], we have observed that the metal center is quite reluctant to be reduced electrochemically, yet they exhibited significant catalytic activity related to the phenoxazinone synthase. We reasoned that the redox potential of the reactants dramatically changes especially when a catalyst-substrate adduct is formed during the course of a redox transformation, and in such a situation facile oxidation of the coordinated *o*-aminophenol by the cobalt(III) center through an inner-sphere electron transfer pathway could be possible. The reduction of the cobalt(III) center in **1** is rather difficult in comparison to its pyridine analogues, as can be reflected from the electrochemical data (Table 3)[18,21]. This is quite probable as the strong electron donating ability of deprotonated pyrrole moiety (compared to neutral pyridine group) significantly increases the stability of the higher oxidation state of cobalt. The inactivity of the present system towards the phenoxazinone synthase activity clearly suggests that, even on coordination of substrate to the metal center, the system is unable to tune the electronic properties of the redox centers significantly so that the oxidation of OAPH by metal center is possible.

In order to justify the experimental facts, we have carried out the DFT studies to compare the electronic structures of the cobalt(III) ions for isomer **III** of complex **1** without methanol to that of the corresponding bis(pyridine-imine) analogues which exhibited significant catalytic activity[21]. These calculations show that the Mulliken charge on Co atom is about +0.626 in the bis(pyridine-imine) ligand system, whereas the charge on Co atom is +0.579 in the present pyrrole-based ligand system (Supplementary Data, Table S3). Although the charge on Co atom is higher in the pyridine complex than in

Table 3—Reduction potentials of complex **1** and the related cobalt(III) complexes reported in literature and rate of the reaction for the oxidation of *o*-aminophenol

Catalyst[a]	Solvent	E_{pc} (V) for Co^{III}/Co^{II}	k_{cat} (h^{-1})	Ref.
$[Co(L)(MeOH)]ClO_4$	Methanol	–0.99	Inactive	This work
$[Co_2(L^1)_2(\mu\text{-}O_2)](ClO_4)_4\cdot 2CH_3CN$	Methanol	–0.583	30.09	21
$[Co_2(L^2)_2(\mu\text{-}O_2)](ClO_4)_4$	Methanol	–0.626	23.04	21
$[Co(L^3)(N_3)_3]$	Methanol	–0.77	20.37	19
$[Co(L^4)(N_3)_3]$	Methanol	–0.57	33.26	19
$[Co_2(amp)_2(\mu\text{-}imp)_2Cl_2]Cl_2\cdot 2H_2O$	Methanol	–0.70	13.75	18

[a] Ligands: L = present ligand; L^1/L^2 = pentadentate ligands derived from Schiff base condensation of N'-(3-aminopropyl)propane-1,3-diamine and 2-pyridinecarboxaldehyde/ 2-acetylpyridine; L^3 = bis(2-pyridylmethyl)amine; L^4 = (2-pyridylmethyl)(2-pyridylethyl)amine; amp = 2-aminomethylpyridine; imp = 2-iminomethylpyridine anion.

the pyrrole analogue, it is not very indicative of lack of oxidizing property of the pyrrole complex. To compare the oxidizing properties we have further calculated the energies of the complexes having overall charge +3 and +2 for pyridine system and +1 and 0 (zero) for pyrrole analogue, i.e., energies of the original and reduced forms of both the systems. It is found that the reduced form (overall neutral) of pyrrole complex is energetically 137.422 kcal mol^{-1} more stable than its oxidized form (overall +1 charge), whereas the reduced form of pyridine complex (overall +2 charge) is about 320.966 kcal mol^{-1} energy more stable than that of oxidized form (overall +3 charge) (Supplementary Data, Table S3). Hence it is reasonable to state that the pyridine complex can oxidized *o*-aminophenol more easily than pyrrole complex. These results conclude that despite the potentially interesting similarities of pyrrole-based ligands to porphyrin systems, the transition metal complexes with the pyrrole-based ligands may not be suitable catalysts for a redox reaction as these complexes are reluctant to be reduced.

Conclusions

We have successfully synthesized and structurally characterized a new mononuclear cobalt(III) complex with a pentadentate Schiff base ligand derived from the condensation of N-(3-aminopropyl)-propane-1,3-diamine with pyrrole-2-aldehyde. X-ray crystallography reveals that the geometry of cobalt(III) ion is a distorted octahedron in which triamine part of the pentadentate ligand occupies the meridional positions, while two pyrrole nitrogen atoms are in *cis* dispositions. DFT study also supports the inferance that the meridional isomer, in which two pyrrole units are in *cis* position, is the most stable isomer. Although the electrospray ionization mass spectral study clearly indicates the formation of a complex-substrate aggregate, the present complex is inactive towards the oxidation of *o*-aminophenol. Inability to oxidize *o*-aminophenol by the present complex can be explained by the electrochemical studies which show that the strong electron donating ability of the deprotonated pyrrole moiety reduces the possibility of reduction of cobalt(III) to cobalt(II). The present study clearly shows that despite the potentially interesting similarities of pyrrole-based ligands to porphyrin systems, the transition metal complexes with the pyrrole-based ligands may not be suitable catalysts for a redox reaction as these complexes are reluctant to be reduced.

Supplementary Data

CCDC 1012497 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or email:deposit@ccdc.cam.ac.uk. Other Supplementary data associated with this article, i.e., Figs S1 and S2, and, Tables S1-S3, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(02)137-144_SupplData.pdf.

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