

Short Communication

Investigation of Electrochemical Property and Crystal Structure of Schiff Base Cobalt(III) Complex

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A Co(III) complex (CoL)Cl·4H₂O was successfully synthesized with a new Schiff base L. Structure analysis reveals that mononuclear cationic complex unit (CoL)⁺ with approximate octahedral geometry of central Co (III) ion existed in the as-prepared cobalt complex. The diameter of cobalt complex nanoparticles after the deposition on glass substrate was found to be around 63nm. In the cyclic voltammetry curves of cobalt(III) complex, two reversible redox waves ascribed to the consecutive redox processes of Co (III)/Co (II) and Co (II)/Co (I) pairs were found, suggesting the successful formation of Co^{III} complex.

Keywords: Cobalt(III) complex; Schiff base; Electrochemical property; Crystal structure; FT-IR

1. INTRODUCTION

3d-Metal complexes, typically synthesized with Schiff base ligands, have attracted enormous attention owing to the remarkable magnetic, catalytic and biological properties. Among the large number of 3d metal ions, Cobalt with the valence state of +3 is of great importance with unusual magnetic and catalytic properties [1-9].

Many oxygenated compounds such as aldehydes, epoxides, ketones and alcohols are high value-added products in the field of chemical and pharmaceutical industries. In general, the oxygen-containing products are prepared by oxidation of olefins. Sulfoxides and sulfones, synthetic intermediates for important organic compounds, are generally synthesized through oxidation of corresponding sulfides with Co(II) salts or its complexes as homogeneous catalysts [10]. Cobalt(III)-peroxo/alkylperoxo species are regarded as intermediates in the oxidation reaction, leading to the

direct use of Co(III) salts as homogeneous catalysts in order to improve the reaction rate [11, 12]. Although the study in Co(III) catalyst is still in initial stage, several Co(III) catalytic systems have already been developed [13-16].

In order to achieve repeated use, supported catalysts which are synthesized via surface functionalization and incorporation of metal complex onto the surface of supports are highly demand [8, 17-23]. Polymer especially chloromethyl polystyrene has opened up new opportunities for the synthesis of supported catalysts [24-27]. Recently, the catalytic activity of massive metal complex such as transition metals coordinated with N, O-containing ligands for various catalytic organic reactions has received a lot of attention and research. However, less attention has been paid to the catalytic activity of polymer that incorporating N, O-donor ligands up to now.

In this study, cobalt (III) complex composed of Schiff base ligand (L) was successfully prepared. The crystallographic structure and electrochemical character of as-prepared cobalt (III) complex was investigated by X-ray diffraction (XRD) and cyclic voltammetry (CV). Then nano-sized cobalt (III) complex was deposited on glass substrate, and the obtained sample was characterized with UV-Vis spectroscopy (UV-Vis) and scanning electron microscopy (SEM).

2. EXPERIMENTS

2.1. Chemicals

Chloromethylated polystyrene, sulfides and alkenes were purchased from Sigma-Aldrich. Cobalt (II) chloride hexahydrate, triethylenetetramine, 2-hydroxyacetophenone and 30% H₂O₂ were supplied by Merck. All reagents and solvents were used as received without subsequent purification.

2.2. Characterizations

¹H NMR spectra of the Schiff base ligand was obtained on Bruker AMX-400 NMR spectrophotometer. Fourier transform infrared (FT-IR) spectra were carried out on Perkin-Elmer FT-IR 783 spectrophotometer with KBr pellets. Electronic spectra were acquired from Shimadzu UV/3101 PC spectrophotometer. Trace GC ultra DSQ II was applied for measuring the mass spectrum of products. Varian AA240 atomic absorption spectrophotometer (AAS) was used to measure the content of cobalt in the sample. Scanning electron microscope (SEM, ZEISS EVO40, England) equipped with EDX was employed to investigated the morphological features of functionalized polystyrene and complex. Cyclic voltammetry measurements were performed using Chi660 (The United States CHI) voltammetric analyzer, a three electrode arrangement made up of a glassy carbon working electrode, a platinum wire auxiliary electrode and a Ag/AgCl reference electrode was used at scan rates of 50 mV/s.

2.3. Synthesis of Schiff base ligand (L)

Schiff base ligand (L) was prepared according to the method reported by Islam et al. [28] with some modification. 20 mL of *N,N'*-bis-(2-aminoethyl)ethylenediamine methanol solution (10 mmol) was added to 20 mL of 2-hydroxyacetophenone methanol solution (20 mmol) and the mixture was refluxed in a water bath for 4 h. Then the resulted dark yellow solution was poured into crushed ice in order to achieve the yellow precipitate. Finally, the achieved solid was rinsed thoroughly with water and then dried. The following related characterizations indicated the successful synthesis of Schiff base ligand (L). $C_{22}H_{30}N_4O_2$ (3.99 g, 88%): calcd. C 69.13, H 7.78, N 14.45 (%); found C 69.08, H 7.81, N 14.42 (%). Mass spectrum (EI): m/z 382 ($M^+ = L^+$). 1H NMR ($CDCl_3$, ppm): δ = 16.12 (s, 2 H, phenolic OH), 7.52–6.88 (m, 8 H), 3.67–3.73 (m, 4 H), 2.75 (t, 4 H), 2.60 (t, 4 H), 2.32 (s, 6 H, methyl), 2.23 (s, 2H, amine). ^{13}C NMR ($CDCl_3$, ppm): δ = 163.4, 160.3, 131.1, 130.5, 123.1, 120.7, 116.5, 49.7, 46.6, 43.3, 14.1.

2.4. Synthesis of cobalt(III) complex (CoL)Cl·4H₂O

A solution of NEt_3 in ethanol (2 mmol) was added slowly to a yellow solution of Schiff base ligand in 30 mL of ethanol (1 mmol). Then a solution of $CoCl_2 \cdot 6H_2O$ in ethanol (1 mmol) was added dropwise to the mixture solution under magnetic stirring. The obtained homogeneous solution was refluxed for 2 h. After cooling down to room temperature naturally, the reaction solution was kept unperturbed in order to evaporate the solvent slowly. Pink single crystal was obtained from mother liquor by filtration after several weeks.

2.5. Synthesis of polymer attached cobalt complex

2 g of chloromethylated polystyrene with the Cl concentration of 5.5 mmol/g and 5.5 mmol of Schiff base ligand (L) were added into 100 mL of DMF in a round bottom flask (250 mL) under stirring, and the obtained mixture was treated with stirring at 100 °C. After 24 h, the reaction solution was filtered. The obtained Schiff base-functionalized polymer was rinsed thoroughly with DMF and dried in vacuum oven for 12 h. 2 g of Schiff base-functionalized polymer was dispersed into 50 mL of ethanol for 30 min. Subsequently, an ethanolic solution of $CoCl_2 \cdot 6H_2O$ (1% w/v) was added to the above solution and the mixture was heated to 70 °C for 6 h. The reaction solution was treated with filtration and the obtained solid was rinsed with ethanol. The resulted polymer impregnated with metal complex was named as PS-TETA-Co 3.

3. RESULTS AND DISCUSSION

Based on XRD spectra, the cobalt complex is composed of mononuclear cationic complex unit $(CoL)^+$ with approximate octahedral geometry of central Co (III) ion and chloride anion for electroneutrality. The coordination spheres of metal ions were found to deviate from the ideal

geometries, which might resulted from the structural constraints caused by the coordinated polydentate ligand. It was found that the *cisoid* and *transoid* angles between nitrogen atoms of imine and Co(III) ion was in the range of 82.97(8)-96.46°(9) and 175.45(8)-178.04°(8), respectively, indicating that the nitrogen atoms of imine bind with each other in *trans* fashion. The *trans* angle (175.45-178.04°) is close to the angle in ideal octahedral geometry (180°). The bond distances of Co-N and Co-O range from 1.876 to 1.9488 Å, which consistent with other similar cobalt (III) Schiff base complexes. The Co-N and Co-O bond distances ranging from 1.876 to 1.9488 Å agree well with similar other Schiffbase complexes of cobalt(III) [29-31]. Table 1 showed the collected crystallographic data and structure refinement parameters. The obtained bond lengths and angles after refinement were shown in Table 2.

Table 1. Crystal data and details of the structure determination.

Formula	C ₂₂ H ₂₈ CoN ₄ O ₂ ·4(H ₂ O),Cl
Formula weight	546.93
Space group	P-1 (no. 2)
a (Å)	10.0667 (12)
b (Å)	10.2854 (13)
c (Å)	13.0365 (18)
α (°)	70.811 (2)
β (°)	70.878 (2)
γ (°)	72.789 (2)
V (Å ³)	1197(3)
Z	2
D (calc) (g/cm ³)	1.51
μ(Mo Kα) (/mm)	0.868
F(0 0 0)	571
Crystal size (mm)	0.04 × 0.08 × 0.10

Table 2. Some selected bond lengths (Å) and bond angles (°) of complex (CoL)Cl· 4H₂O.

Co1 -O1	1.902(16)	Co1 -O2	1.856(19)
Co1 -N1	1.909(2)	Co1 -N3	1.906(2)
Co2 -N3	1.943(2)	Co1 -N3	1.937(4)
O1 -Co1 -O2	87.04(7)	O1 -Co1 -N1	87.51(7)
O1 -Co1 -N3	89.17(7)	O1 -Co1 -N1	166.65(7)
O2 -Co1 -N4	92.36(8)	O2 -Co1 -N2	84.10(9)
O2 -Co1 -N2	92.45(8)	O2 -Co1 -N2	93.32(9)

Cyclic voltammetry (CV) curves were achieved to investigate the electrochemical character of Co (III) complex. Specific experimental parameters were as follows: tetrabutylammonium perchlorate dissolved in DMF solution (0.05 M) as electrolyte, 100 mV/s as scanning rate and -2 to 0.5 V (vs. Ag/AgCl) as potential range. As can be seen from the obtained cyclic voltammetry (CV) curves for Co(III) complex (Fig. 1), two pairs of reversible redox waves could be found, which belonged to the consecutive redox processes of Co(II)/Co(I) and Co(III)/Co(II) pairs. As to the first pair of redox wave which was ascribed to the redox process of Co (III)/Co (II), the peak potentials were 0.132 V (E_{pa1}) and -0.879 V (E_{pc1}), respectively, and thus the gap between anodic and cathodic peak (ΔE_{p1}) was 1.011 V. The proportional of cathodic peak current to anodic peak current (i_{pc1}/i_{pa1}) was calculated to be 1.412. Similarly, the second pair of redox wave which was ascribed to the redox process of Co (II)/Co (I), the peak potentials were -0.799 V (E_{pa2}) and -1.541 V (E_{pc2}), respectively, and thus the gap between anodic and cathodic peak (ΔE_{p2}) was 0.742 V.

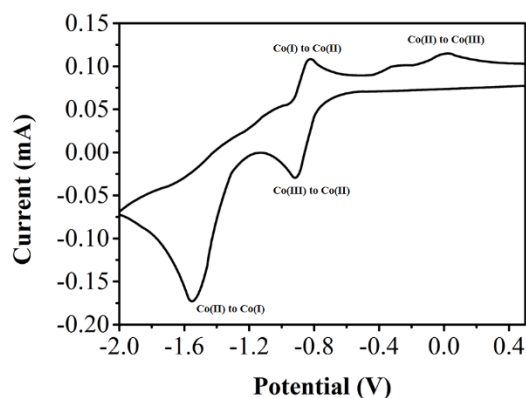


Figure 1. Cyclic voltammogram of $(CoL)Cl \cdot 4H_2O$ complex. Condition: scan rate: 50 mV/s; electrolyte: 0.05 M DMF.

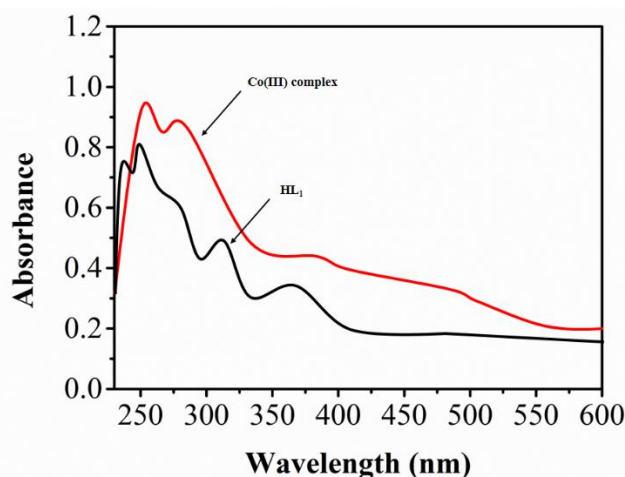


Figure 2. UV-vis absorption spectra of L and $(CoL)Cl \cdot 4H_2O$.

The proportional of cathodic peak current to anodic peak current (i_{pc2}/i_{pa2}) was calculated to be 0.723. The electrode reaction was verified to be quasi-reversible [32]. In addition, the two reversible

redox waves were found to be ascribed to the consecutive redox processes of Co (III)/Co (II) and Co (II)/Co (I) pairs, affirming the successful formation of Co^{III} complex [33-37].

UV-vis absorption spectra of L and (CoL)Cl·4H₂O were measured by dissolving samples in 0.05 mM CH₂Cl₂ solution and the results were given in Fig. 2. As can be seen from the UV-vis absorption spectrum of L, three absorption peaks were observed at 242, 303 and 366 nm, respectively. The absorption spectrum of (CoL)Cl·4H₂O was different from that of L. Firstly, the absorption peak at 366 nm was found to be absent in (CoL)Cl·4H₂O. Secondly, the absorption peak at 242 nm exhibited a shift to 248 nm and 269 nm for (CoL)Cl·4H₂O. In addition, a new obscure absorption peak at 453 nm was found in the absorption spectrum of (CoL)Cl·4H₂O, which could be ascribed to the d-d transition of Co(III) ion. The intense band around 453 nm corresponded to ligand-to-metal charge transfer (LMCT) transitions [38]. The Co(III) complex with 3d⁶ electronic configuration belonged to ⁴T_{1g}(F) → ⁴T_{1g}(P) d-d transition of six coordinated Co(III) ion [39]. Co (III) ion was verified to be in octahedral geometry as indicated by the spin-allowed d-d bands. In addition, the d-d electronic transition was caused by the splitting of 3d levels in coordination compounds. All the results herein were similar to the spectral signature of transition state metal complexes. These absorptions also present in the spectrum of the cobalt complex but shifted which indicates the coordination behavior of the polymer anchored Schiff base ligand to the metal ion. Polymer anchored cobalt complex shows an additional band at 625–700 nm which can be assigned to d→d transition [40].

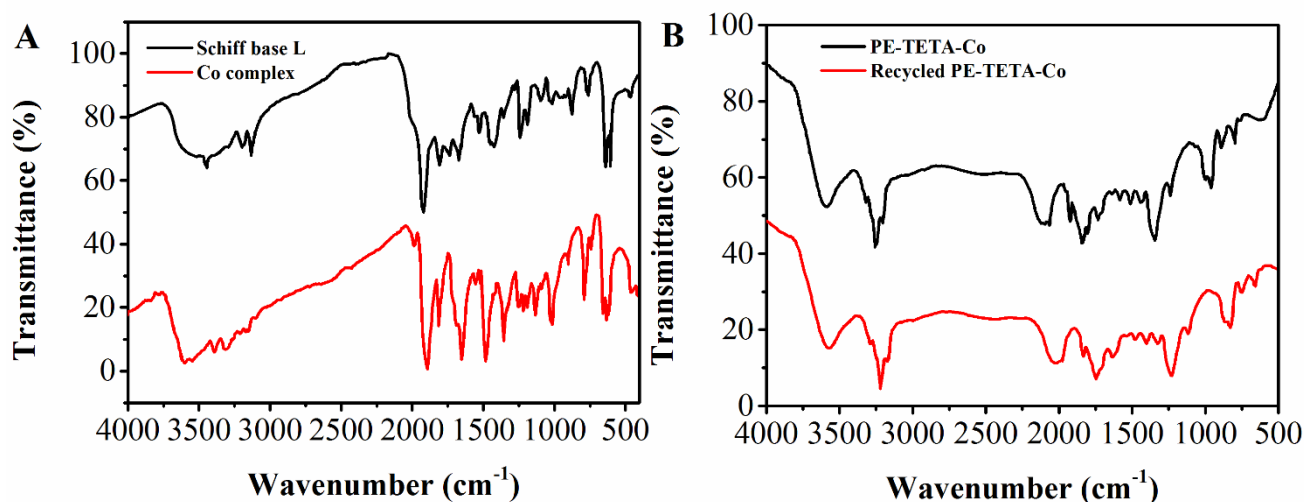


Figure 3. (A) FT-IR spectra of Schiff base L and cobalt complex (CoL)Cl·4H₂O. (B) FT-IR spectra of polymer, polymer supported Schiff base ligand and polymer supported cobalt complex.

Fig. 3A showed the FT-IR spectra of Schiff base ligand (L) and cobalt complex (CoL)Cl·4H₂O. A sharp peak at 1612 cm⁻¹ was observed in Schiff base ligand (L), which could be ascribed to the C=N functionality. This sharp peak shifted from 1612 cm⁻¹ to 1591 cm⁻¹ for cobalt complex, indicating the successful coordination of Schiff base to central Co(III) ion via azomethine nitrogen. In addition, a strong band in the region 3310-3390 cm⁻¹ was found in Schiff base ligand (L), which was resulted from the stretching vibration of -NH (secondary amine) and -OH. The phenolic (C-O) stretching frequency of cobalt complex shifted to higher frequency at 1320 cm⁻¹ in comparison with that of

ligand L (1280 cm^{-1}), demonstrating the coordination of metal through phenolic oxygen. The peak observed at 1493 cm^{-1} for L corresponds to N-H (secondary amine) bending vibration. However, this peak was absent in $(\text{CoL})\text{Cl}\cdot 4\text{H}_2\text{O}$, indicating the absence of N-H (secondary amine) bond in cobalt complex. Moreover, the bands at 3465 and 1540 cm^{-1} was resulted from the $\nu(\text{OH})$ stretching of lattice water molecule in the cobalt complex.

FT-IR spectra of polymer, polymer supported Schiff base ligand and polymer supported cobalt complex was investigated and the results were shown in Fig. 3B. Owing to the low concentration of complex, the intensity of polymer supported metal complex was weak. As shown from the FTIR spectrum of polymer supported metal complex, a band at 1660 cm^{-1} ascribed to C=N bond of polymeric support was observed. In addition, a sharp peak at 1263 cm^{-1} ascribed to C-Cl bond of $-\text{CH}_2\text{Cl}$ group in polymer weaken after the load of Schiff base on polymer support. The two phenomenons mentioned above confirmed the successful loading of Schiff base (L) on polymer matrix. The N-H (secondary amine) bending vibration (1487 cm^{-1}) observed in L was found to be absent in the polymer supported Schiff base ligand, indicating that the attachment of Schiff base (L) to polymer was carried out via secondary amine 'N' atom. The frequency of phenolic (C-O) stretching in polymer anchored ligand was observed at 1366 cm^{-1} . The bands ascribed to C=N and phenolic (C-O) was found to shift to lower and higher frequency region after complexation, respectively.

The morphology feature of nano-sized $(\text{CoL})\text{Cl}\cdot 4\text{H}_2\text{O}$ complex was investigated by SEM after the deposition of complex on glass substrate and the results were shown in Fig.4 . The cobalt complex molecules could be dispersed uniformly into nanoparticles after the deposition on glass substrate. The diameter of nano-sized $(\text{CoL})\text{Cl}\cdot 4\text{H}_2\text{O}$ complex was found to be around 63nm. The aggregation of nano-sized particles still existed as indicated from SEM images.

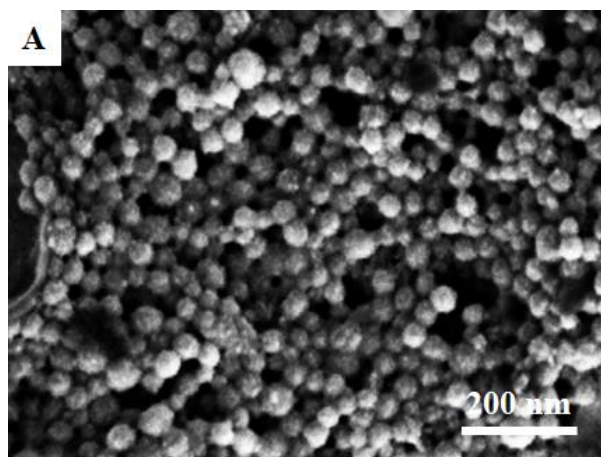


Figure 4. SEM top view image of nano-sized $(\text{CoL})\text{Cl}\cdot 4\text{H}_2\text{O}$ complex.

The electrochemical behaviors were then examined in aqueous solutions at pH 4.0–7.0, a range associated with catalytic water reduction. In the cathodic scan an irreversible wave can be seen at -1.40 V , where the peak position varied with solution pH. This is most likely due to water reduction, and the potential shifts anodically with decreasing pH. The electro-catalytic activity was also evaluated by bulk electrolysis of $1.1 \times 10^{-6}\text{ M}$ complex 1 in 0.25 M buffer. At the applied potential of -1.40 V

versus Ag/AgCl, the maximum charge was only 47 mC in 2 min of electrolysis in the absence of complex 1 (Fig. 5).

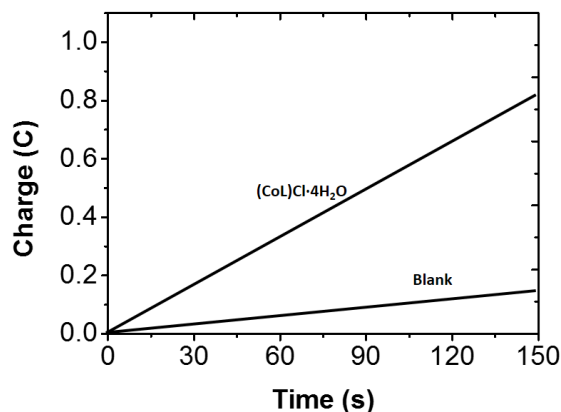


Figure 5. Charge buildup of 0.25 M phosphate buffer and (CoL)Cl·4H₂O complex at pH 7.0.

4. CONCLUSIONS

Nano size (CoL)Cl·4H₂O complex was successfully prepared with the employment of a new Schiff base ligand (L). Cyclic voltammograms curves of (CoL)Cl·4H₂O complex demonstrated the quasi-reversible redox process of Co(III)/Co(II) and Co(II)/Co(I) pairs. Co (III) ion was verified to be in octahedral geometry as indicated by the UV-vis absorption spectrum. FTIR spectrum of polymer supported cobalt complex indicated that Schiff base (L) was attached to polymer via secondary amine 'N' atom. The diameter of as-prepared nano-sized (CoL)Cl·4H₂O complex was found to be around 63 nm.

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