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Synthesis and characterization of chromium(III) complexes derived from tridentate ligands: Generation of phenoxyl radical and catalytic oxidation of olefins

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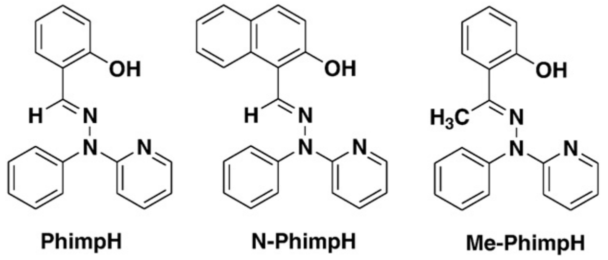
ABSTRACT

The mononuclear chromium complexes $[Cr(Phimp)_2](ClO_4)$ (**1**), $[Cr(N–Phimp)_2](ClO_4)$ (**2**), and $[Cr(Me–Phimp)_2](ClO_4)$ (**3**) (where PhimpH = (2-((2-phenyl-2-(pyridin-2-yl)hydrazono)methyl)phenol), N–PhimpH = (2-((2-phenyl-2-(pyridin-2-yl)hydrazono)methyl)napthalen-1-ol), Me–PhimpH = (2-(1-(2-phenyl-2-(pyridine-2-yl)hydrazono)ethyl)phenol) where H stands for dissociable proton) were synthesized and characterized spectroscopically. Electrochemical studies were investigated for the stabilization of Cr(III) complexes and electrochemically generation of phenoxyl radical complexes. Phenoxyl radical complexes were also generated by ceric ammonium nitrate (CAN) and characterized by UV–visible spectra. The complexes were evaluated for their activity as catalysts for the epoxidation of olefins. The chromium complexes catalyzed epoxidation of olefins, viz. styrene, *cis*-cyclooctene and *trans*-stilbene with hydrogen peroxide (H_2O_2) as terminal oxidant, to give corresponding epoxides and oxidative products at ambient temperature.

Catalysis is known to play a key role in modern chemical technologies. Nowadays it is generally agreed that the key role in catalytic reactions is played by intermediate chemical interaction of reactive molecules with definite functional groups (active sites) of homogeneous, heterogeneous or biological catalysts (enzymes) [1]. Asymmetric oxidation of hydrocarbons under mild and environmental friendly conditions is an important research field, since industrial processes, especially in the pharmaceutical industry, for synthesizing synthons from readily available olefins [2]. However, selective oxidation of alkenes under mild conditions is a difficult task due to their chemical inertness. In this regard, use of coordination complexes of transition metals as catalysts is of abiding importance as it offers an effective possibility for synthesis of pure compounds [3,4]. Although transition metal Schiff base complexes of bear resemblance to enzymatic catalysts and are eye-catching since they provide advantages due to their relatively easy synthesis and versatile coordination structures [5–9]. In this regard, first row transition metals namely vanadium, chromium, iron and copper complexes are preferred because of their versatile coordination chemistry in different oxidation states [10]. Moreover, these transition metal-catalyzed oxidation reactions are chemical models for the monooxygenase, cytochrome P-450 enzymes [11,12].

Hence chromium is an important metal for catalytic studies because chromium exhibited variable oxidation states, spin states, coordination numbers and redox properties in different chromium complexes [13]. However, chromium(III) is an essential nutrient that is involved in the glucose tolerance factor (GTF) in maintenance of normal carbohydrate and lipid metabolism [14,15]. Schiff base complexes of chromium(III) such as N,N′-ethylene bis(salicylidene-iminate)diaquochromium(III) chloride, $[Cr(salen)(H_2O)_2]Cl$ were used as a new model of GTF [16,17]. Chromium–salen complexes are well-known catalysts, both in heterogeneous and homogeneous systems. Other applications of theses complexes are reported, such as, the stereoselective alkene epoxidations [18,19] and alcohol oxidations [20]. There is a wide range of chromium complexes that are known to be capable of catalyzing asymmetric oxidation of unfunctionalized olefins as well as other organic molecules in presence of terminal oxidants, reports on the use of chromium complexes are sparse in the literature [3,4,21–24].

Herein we report the synthesis and characterization of chromium complexes $[Cr(Phimp)_2](ClO_4)$ (**1**), $[Cr(N–Phimp)_2](ClO_4)$ (**2**), and $[Cr(Me–Phimp)_2](ClO_4)$ (**3**) derived from tridentate ligands PhimpH, N–PhimpH and Me–PhimpH respectively having NNO donors (Scheme 1). Electrochemical studies were also investigated for the stabilization of



Scheme 1. Schematic drawing of tridentate Schiff's base ligands and their abbreviations.

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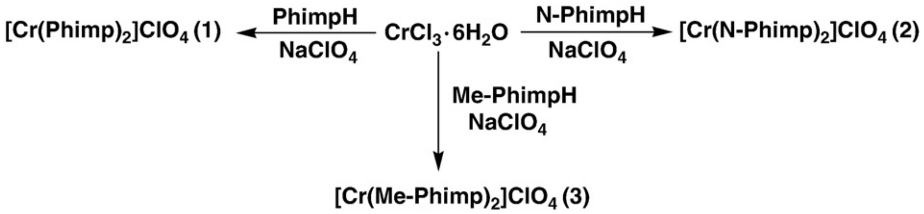

Scheme 2. Schematic synthetic procedure of complexes **1–3**.

Cr(III) oxidation states. Phenoxyl radical complexes are important intermediates in the catalytic oxidation of primary alcohol to aldehyde and aldehyde to carboxylic acid by galactose oxidase (GO) [25,26] and glyoxal oxidase [27] enzymes respectively. Due to the presence of phenolato function in the ligand frame we have explored the generation of phenoxyl radical complexes. The catalytic oxidation chemistry of olefins by the chromium complexes was examined.

The tridentate ligands PhimpH, N-PhimpH and Me-PhimpH were synthesized by the reported procedure [28]. Complexes were synthesized by the stirring of ligands with chromium(III) salt $CrCl_3 \cdot 6H_2O$ in ethanol for 6 h. Bis complexes were obtained even though reaction was started by 1:1 ratio of ligand and salts or 2:1 ratio. Details of the syntheses are summarized in Scheme 2.

The characteristic band of azomethine ($\nu_{\text{-HC=N}}$) group in IR spectra of the ligands were observed near 1607–1611 cm^{-1} [29]. Coordination of the nitrogen to the metal center reduced the electron density in the azomethine moiety and thus lowered the ($\nu_{\text{-HC=N}}$) frequency. Decrease in stretching frequencies for ($\nu_{\text{-HC=N}}$) in complexes **1, 2** and **3** clearly indicated the ligation of azomethine nitrogen (—HC═N–) to metal center [30,31]. The bands near 1090 cm^{-1} together with a band at 623 cm^{-1} were found in all chromium(III) complexes **1**–**3** which showed the presence of perchlorate ion. The lack of splitting of these two bands suggested the presence of non-coordinated perchlorate ion to the metal center [30,31]. A high intensity band near 1300 cm^{-1} in the Schiff's bases can be assigned as phenol C–O ($\nu_{\text{C-OPh}}$) stretching frequency. Shift of $\nu_{\text{C-O}}$ to higher frequency supported the deprotonation of phenolate function and the formation of metal oxygen bond [32]. It was further supported by disappearance of the broad $\nu_{\text{O-H}}$ band in IR spectra of all metal complexes. The absorption spectra of complexes were recorded in acetonitrile at room temperature (Fig. S1). The transition band near 235–245 nm was designated as π–π* transition in ligand (Table 1). The band near 420 nm for complexes **1**, **2** and **3** was assigned as ligand-to-metal charge transfer (LMCT) transition of phenolato oxygen to chromium(III) [33]. However, in addition **2** possesses one absorption band ~450 nm which was also of charge transfer type. The molar conductivity measurements in dimethylformamide at *ca.*10^{-3} M determined at 298 K for complexes were found to be 48–59 $\Omega^{-1}cm^2mol^{-1}$. These values confirmed the uni-univalent (1:1) electrolyte behavior in solution [34]. For complexes, magnetic moments were measured at room temperature (300 K) (Table S1). Complexes were paramagnetic in nature and stabilized the $3d^3$ system [35].

Electrospray ionization of methanolic solution of $[Cr(Phimp)_2](ClO_4)$ (**1**), $[Cr(N\text{–}Phimp)_2](ClO_4)$ (**2**) showed intense signals corresponding to $[Cr(Phimp)_2]^+$ ($m/z = 628$) and $Cr(N\text{–}Phimp)_2]^+$($m/z = 728$) respectively after losing the ClO_4^- appeared as the leading cationic species. Representative ESI-MS spectra for $[Cr(Phimp)_2](ClO_4)$ (**1**), $[Cr(N\text{–}Phimp)_2](ClO_4)$ (**2**) are presented in Figs. S2 and S3.

The redox potentials of complexes **1**–**3** are described in Table 1 and representative voltammograms are shown in Fig. 1 and Figs. S4–S5. The neutral uncomplexed ligands did not show any cyclic voltammogram over the range from 0.0 to 1.1 V; hence all the curves were attributed to the redox activity of our complexes. Complexes **1** and **2** showed quasi-reversible peaks and from the Table 1, it has been shown that one electron is involved in this redox process. The wave detected at 0.12–0.92 V vs. Ag^+/AgCl has been considered as one-electron-redox process attributed to the reduction of $[Cr^{III}L_2]^+$ to $[Cr^{II}L_2]$ (where L = $Phimp^-$, N-$Phimp^-$) indicating Cr(III)/Cr(II) redox couple. On the other hand, complex **3** showed irreversible peak at −1.3 V (Fig. S5). We want to mention here that for complex **2**, we found small peaks at ~−0.75 V and +0.5 V during our scan from −1.4 V to +1.4 V vs. Ag/AgCl. If we

Table 1
Electronic spectra and cyclic voltammetric redox potentials of complexes **1**–**3** and their phenoxyl radical species.

Complex[a]	λ_{max}/nm (ε/M^{-1} cm^{-1})][b]	[Cr(III)/Cr(II)][c]$E_{1/2}$[d]/V (ΔE[e]/V)
1	427(8700), 338 (18,200), 302 (21,400), 244 (37,900)	0.123(0.064)
$[1]^{\bullet+}$	601(420), 551(720), 422(8800), 336(18,280), 300(22,600), 246(36,800)	–
2	484 (4300), 445 (7900), 426 (7400), 350 (16,600), 257 (32,400), 244 (34,600)	0.92(0.112)
$[2]^{\bullet+}$	805(600), 672(360), 444(12,020), 424(11,940), 349(24,040)	1.20(0.093)
3	409 (7300), 354 (10,300), 308 (15,800), 235 (42,300)	–
$[3]^{\bullet+}$	740(100), 560(420), 399(6,100), 311(14,140), 268(23,960)	–

[a] All complexes in parentheses are radical species.
[b] Solvent: acetonitrile.
[c] Conditions: solvent dichloromethane; supporting electrolyte, TBAP (0.1 M); working electrode glassy carbon; reference electrode, Ag/AgCl; scan rate 0.1 V/s, concentration ~10^{-3}M at 298 K.
[d] $E_{1/2} = 0.5(E_{pa} + E_{pc})$.
[e] $\Delta E = (E_{pa} - E_{pc})$ where E_{pa}, E_{pc} are anodic and cathodic peak potential.

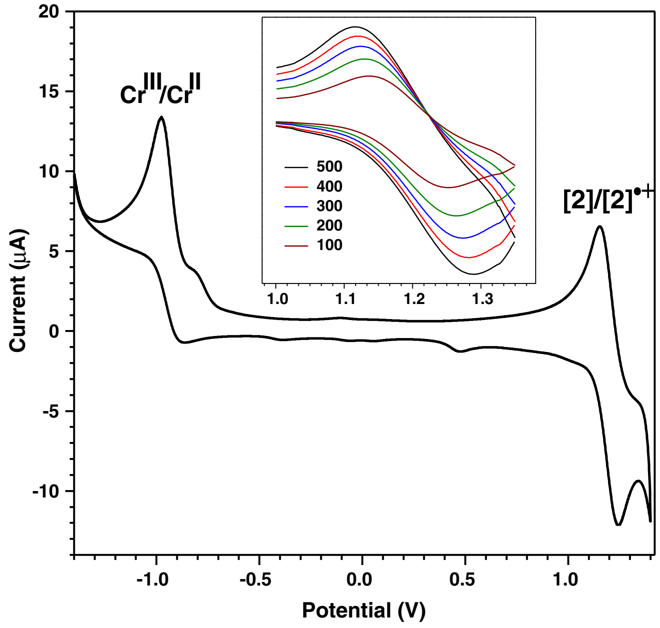

Fig. 1. Cyclic voltammograms of a 10^{-3} M solution of complex **2**: using working electrode: glassy-carbon, reference electrode: Ag^+/AgCl; auxiliary electrode: platinum wire, scan rate 0.1 V/s. Inset: Cyclic voltammograms at100–500 mV/s scan rates.