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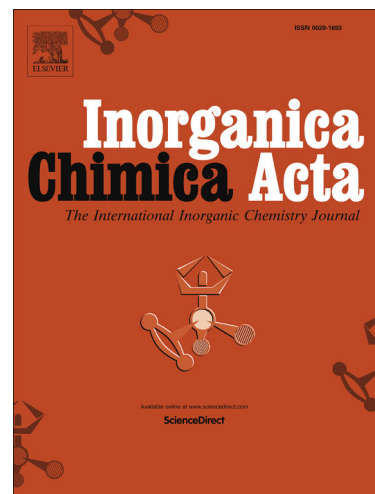
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Synthesis, characterization and catalytic activity of new Cr(III) complex in oxidation of primary alcohols to aldehydes

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Abstract

New mononuclear complex of chromium(III), $[\text{Cr}(\text{bp})(\text{N}_3)(\text{CH}_3\text{OH})] \cdot 2\text{CH}_3\text{OH}$ has been synthesized where H_2bp is *N,N*-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)-*N',N'*-dimethylethylene-1,2-diamine. The complex was characterized by elemental analyses and spectroscopic methods and X-ray diffraction analysis. Single crystal X-ray diffraction structure analysis of the complex revealed that the chromium ion is octahedrally coordinated where the bis(phenolate) ligand (bp^{2-}) is N_2O_2 -bonded to the Cr(III) center in a tetradentate dinegative fashion. The catalytic potential of this complex has been tested for the oxidation of primary alcohols using H_2O_2 as oxidant. The effects of various parameters including molar ratio of oxidant to substrate, temperature, and solvent have been studied. Excellent conversions have been obtained for the oxidation of benzyl alcohols containing electron-donating groups on *para*-position.

Keywords: Bis(phenolate) ligands; Cr(III) complex; Catalytic oxidation; Crystal structure; Oxidation of alcohols

1. Introduction

The oxidation of alcohols is an important process in organic synthesis [1]. The chemo-, regio-, and stereoselective oxidation of alcohols to corresponding carbonyl compounds is one of the fundamental organic transformations from the synthetic point of view [2]. However, the selective oxidation of primary alcoholic compounds to corresponding aldehydes remains very difficult because in the oxidation of primary alcohols, the main products are the corresponding carboxylic acids [3]. Many reagents and various methods are known for selective oxidation of primary alcohols. Catalytic oxidation of alcohols using transition metal complexes such as V [4], Cu [5], Mo, W [6], Ru [7], Pd [8], Mn [9], *etc.* is one of the most important methods for obtaining carbonyl compounds [10].

While many metal complexes catalytically convert alcohols to carbonyl compounds, chromium compounds are particularly useful for this process [11]. So far chromium based materials are used for oxidation of alcohols. Chromic acid [12], the Jones reagent (chromium trioxide/H₂SO₄) [13], the Collins reagent (chromium trioxide/pyridine complex) [14], pyridinium chlorochromate (PCC) [15], poly(vinylpyridinium) chlorochromate (PVPCC) [16], and pyridinium dichromate (PDC) [17] are some of the more popular commercially available chromium based oxidants used for such transformations. Nevertheless, there are few reports on catalytic oxidation of alcohols in presence Cr(III) complexes [18]. Recently, Cr(III) complexes have been employed as both homogenous [19] and heterogeneous [20] catalysts for epoxidation of olefins. Also, they have been used as catalyst in selective oxidation of alcohols using iodobenzene (PhIO) as the oxygen source [21]. The use of hydrogen peroxide in the

oxidation of organic molecules is a major goal, both in academic and in industry. This is related to the environmental acceptability of this oxidant, which depends mainly on the nature of its byproduct (water) [22]. Cr(III) complexes also show considerable catalytic activity in the presence of H₂O₂ as oxidant [23].

Considering the effect of bulky *tert*-butyl group as directing substituent for selective oxidation reactions [24,25], in the present work, we report synthesis, characterization, crystals structure and catalytic reactivity of new chromium(III) complex of tetradentate ligand including two phenolic rings bearing bulky *tert*-butyl substituents at the *ortho*- and *para*- positions relative to the phenolic oxygen (Scheme 1). This ligand has been prepared by simple one-pot reaction from the Mannich condensation of 2,4-di-*tert*-butylphenol, formaldehyde and *N,N*-dimethylethane-1,2-diamine. The catalytic reactivity of this complex has been investigated in oxidation of primary alcohols in the presence of H₂O₂.

Scheme 1.

2. Experimental

2.1. Material and instruments

All starting chemicals were commercially available reagents and were used without further purification. IR spectra were recorded in KBr discs with a Bruker FT-IR spectrophotometer. UV-Vis solution spectra were recorded using a thermo-spectronic Helios Alpha spectrometer. ¹H and ¹³C NMR spectra were measured with a Bruker Spectrospin spectrometer at 250 and 62.5 MHz, respectively. The reaction products of oxidation were determined and analyzed by HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 μm × 320 μm × 0.25

μm) and gas chromatograph-mass spectrometry (Hewlett-Packard 5973 Series MS-HP gas chromatograph with a mass-selective detector). The elemental analyses (carbon, hydrogen and nitrogen) of compounds were obtained from Carlo ERBA Model EA 1108 analyzer. Chromium percentage of complex was measured by Varian spectrometer AA 220 equipment.

2.2. Synthesis of *N,N*-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)-*N',N'*-dimethylethylene-1,2-diamine (*H₂bp*)

For the synthesis of bis(phenolate) ligand, *H₂bp* (Scheme 1a), methanol (35 mL) was added to *N,N*-dimethylethane-1,2-diamine (5.40 mL, 0.05 mol) and the rapidly stirred solution was cooled to 0 °C. Then aqueous formaldehyde solution (37wt.% in H₂O, containing 10% methanol as stabilizer, 8 mL, 0.1 mol) was added dropwise. The mixture was stirred for 15 minutes, then 2,4-di-*tert*-butylphenol (20.63 g, 0.1 mol) was added and the mixture was refluxed for 48 h. At the end, the solution was evaporated on a steam bath to 5 mL and cooled to room temperature. Resulting white precipitate was separated and filtered off, washed with 20 mL of cooled methanol and re-crystallized. Yield 80% (20.99 g). M.p. 131-133 °C. *Anal.* Calc. for C₃₄H₅₆N₂O₂ (MW = 524.82): C, 77.81; H, 10.76; N, 5.34. Found: C, 77.84; H, 10.80; N, 5.30. FT-IR (KBr, cm⁻¹): 3188 (s, br), 2950 (m, br), 2865(m, br), 1768(s), 1605(m), 1592(w), 1571(s), 1506(m), 1483(s), 1467(m), 1417(m), 1388(m), 1374(m), 1360(m), 1303(m), 1285(m), 1256(m), 1224(w), 1202(w), 1160(m), 1121(m), 1105(s), 1086(w), 1057(w), 1043(s), 1024(m), 987(s), 948(m), 938(m), 923(s), 910(w), 891(w), 879(s), 824(m), 813(m), 800(w), 782(m), 756(m), 725(m), 681(m), 665(w), 649(m), 540(m). ¹H NMR (250.13 MHz, CDCl₃, 25

°C, TMS, ppm): δ = 1.36 (s, 18 H, CH₃ of *t*-Bu), 1.38 (s, 18 H, CH₃ of *t*-Bu), 2.30 (s, 6H, CH₃ of N(CH₃)₂), 2.42 (t, 2 H, J = 7.0 Hz, (CH₃)₂N-CH₂), 2.57 (t, 2H, J = 7.0 Hz, N-CH₂), 3.81 (s, 4H, Ar-CH₂), 6.94 (d, 2H, $^4J_{HH}$ = 2.0 Hz, aryl), 7.11 (d, 2H, $^4J_{HH}$ = 2.0 Hz, aryl), 9.16 (s, 2H, OH). ¹³C NMR (62.19 MHz, CDCl₃, 25 °C, TMS, ppm): δ = 31.2 (CH₃ of *t*-Bu), 31.4 (CH₃ of *t*-Bu), 34.5 (C of *t*-Bu), 35.2 (C of *t*-Bu), 45.5 (CH₃ of N(CH₃)₂), 54.2 (2Ar-CH₂), 54.4 (CH₂-N), 57.8 (CH₂-NMe₂), 121.2, 122.7 (4CH of aromatic), 128.6, 136.5, 141.2, 154.8 (8C of aromatic). UV-Vis (5×10^{-5} M, CH₃OH): λ_{\max} (ϵ , M⁻¹ cm⁻¹) = 216 (33 000), 279 nm (9 100).

2.3. Synthesis of [Cr(bp)(N₃)(CH₃OH)]·2CH₃OH (**1**)

The appropriate amount of ligand H₂bp (0.524 g, 1 mmol) and NaN₃ (0.13 g, 2.00 mmol) was dissolved in CH₃OH in the presence of CrCl₃·6H₂O (0.532 g, 2.00 mmol). The solution was gently refluxed for 6 h. After cooling, the resulting solid was filtered off, washed with cooled absolute ethanol and dried at 100 °C. Single crystals of [Cr(bp)(N₃)(CH₃OH)]·2CH₃OH were obtained by thermal gradient method. Yield 70% (0.49 g). *Anal.* Calc. for C₃₇H₆₆CrN₅O₅ (MW = 712.95): C, 62.33; H, 9.33; N, 9.82; Cr, 7.29%. Found: C, 62.36; H, 9.35; N, 9.79; Cr, 7.32%. FT-IR (KBr, cm⁻¹): 3419 (OH, w, br), 2955 (CH alif., s), 2924(s), 2854(w), 2063 (N₃, vs), 1634(m), 1599(m), 1478(m), 1470(m), 1443(m), 1435(m), 1414(w), 1386(w), 1362(m), 1297(m), 1254(w), 1237(m), 1165(w), 1094(w), 1018(m), 876(m), 838(w), 758(w), 747(w), 668(w), 553(w). UV-Vis (2.5×10^{-5} M, CH₃OH): λ_{\max} (ϵ , M⁻¹ cm⁻¹) = 216 (35 200), 279 nm (6 300).

2.4. X-ray Crystallography

Data collection for X-ray structure determination was performed on a Kuma KM4-CCD automated four-circle diffractometer with a Sapphire 2 CCD detector using graphite monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 100(2) K (Oxford Cryosystems cooler). Data collection, cell refinement, and data reduction and analysis were carried out with CrysAlisCCD and CrysAlisRED, respectively [26]. Diffraction data have been corrected for absorption effects by multi-scan [26]. The structure was solved by direct methods using SHELXS-97 [27], and refined by a full-matrix least squares technique on F^2 with SHELXL-2013 [27]. All H atoms were found in difference Fourier maps (except for those from disordered *t*-Bu group), and in the final refinement cycles they were repositioned in their calculated positions and refined using a riding model, with C—H = 0.95–0.99 \AA and O—H = 0.84 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{CH}, \text{CH}_2)$ or $1.5U_{\text{eq}}(\text{O}, \text{CH}_3)$. One of the *t*-Bu groups of the bp^{2-} ligand and N_3^- anion were found to be disordered, and were refined in two sites each, with s.o.f. = 0.757(9) and 0.243(9) for bp^{2-} , and 0.579(14) and 0.421(14) for N_3^- . In the refinement procedure of the disordered regions, some geometrical restrains and constraints on the fractional coordinates and anisotropic displacement parameters (SAME, EXYZ, EADP instructions in SHELXL-2013) were applied; for details see CIF file. All partially occupied atoms were refined isotropically. The structure plots for complex **1** were prepared with DIAMOND [28]. The crystal data and refinement parameters are presented in Table 1.

Table 1.

2.5. Experimental set up for catalytic oxidation

Liquid phase catalytic oxidations of alcohols were carried out under air (atmospheric pressure) in a 25 mL round bottom flask equipped with a magnetic stirrer. In a typical experiment, H₂O₂ was added to a flask containing the catalyst (1.40×10^{-3} mmol) benzyl alcohol (1 mmol), and 1.0 mmol *n*-octane as internal standard in a solvent (3 mL). The course of the reaction was monitored by injection of 1 μ L of reaction mixture (picked from organic phase) to a gas chromatograph equipped with a capillary column and a flame ionization detector. The oxidation products were identified by comparing their retention times with those of authentic samples or alternatively by TLC, ¹H NMR and GC–Mass analyses. Control reactions were carried out in the absence of catalyst, under the same conditions as the catalytic runs and indicated there was no products in the absence of catalyst.

3. Results and discussion

3.1. Synthesis of ligand and Cr-complex (I)

The reaction of *N,N*-dimethylethane-1,2-diamine with 2,4-di-*tert*-butylphenol in the presence of formaldehyde gave the desired tetradentate bis(phenolate) ligand, H₂bp, in excellent yield and purity (Scheme 1a). The formation of the ligand, H₂bp, has been confirmed by NMR and infrared spectroscopy. In the IR spectrum of the ligand the bands at 3188, 1592 and 1256 cm⁻¹ are due to O–H, C=C and C–O_{phenolic} stretches, respectively [29]. The elemental analysis is in good accordance with the proposed structure. The Cr(III) complex of bp²⁻ ligand was slowly formed by the reaction of H₂bp with chromium(III) chloride in the presence of pseudohalide coligand (N₃⁻) in methanol

(Scheme 1b). On complexation the shift of C–O_{phenolic} and C–N bands show coordination of H₂bp as tetradentate dianionic ligand. In the IR spectrum of [Cr(bp)(N₃)(CH₃OH)]·2CH₃OH (**1**) the strong band at 2055 cm⁻¹ is assigned to $\nu(\text{N}_3)$ [30], this band is observed as a new peak for the complex and is not present in the spectrum of the free ligand. The electronic spectra of complex **1** (green) and H₂bp (colorless) in methanol solutions are shown in Fig. S1. The bis(phenolate) ligand displays two absorption bands at 216 and 279 nm. Based on their extinction coefficients they are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. The electronic spectrum of the complex is very similar to the spectrum of the ligand and the absorption bands are attributed to the intraligand $\pi \rightarrow \pi^*$ (216 nm) and $n \rightarrow \pi^*$ (279 nm) transitions. A little difference in shape of spectrum indicates the coordination of the ligand to the Cr(III) ion.

3.2. X-ray structure of complex [Cr(bp)(N₃)(CH₃OH)]·2CH₃OH (**1**)

The Cr-complex of the bp²⁻ ligand crystallizes as a methanol disolvate, [Cr(bp)(N₃)(CH₃OH)]·2CH₃OH (**1**). The crystal structure of **1** determined by X-ray analysis is shown in Fig. 1, and selected bond lengths and bonding angles are tabulated in Table 2. X-ray analysis of **1** reveals that this compound is a neutral mononuclear complex of Cr(III). The coordination environment around the Cr(III) center is best described as a distorted octahedral *mer*-[CrO₃N₃], formed by two nitrogen atoms and two oxygen atoms provided by the bis(phenolate) ligand, one nitrogen atom from the azide co-ligand and an oxygen atom from coordinated methanol molecule. In complex **1**, two phenolate donor atoms provided by bis(phenolate) ligand are located in a *trans* mode towards each other. The N1 atom and two phenolate oxygen atoms, together with the nitrogen atom of azide

ligand form the basal plane. The methanol oxygen atom occupies an axial position at a distance of 2.029(3) Å. Remaining axial position in the complex is occupied by nitrogen atom of *N,N*-dimethyl moiety, with the length of Cr1–N2 bond equal to 2.140(4) Å. In complex **1** the azide ligand show asymmetric N–N distances (N3–N4/N4–N5) of 1.207(6)/1.162(7) Å and the N3–N4–N5 angle is 177.3(12)°, which is typical shape of the azide ligand [31]. There are some strong and directed hydrogen bonding in the crystal lattice of the complex. Uncoordinated methanol molecules are tightly linked with the complex molecules *via* both O–H···O and O–H··· π contacts, as shown in Fig. S2 and Table S1.

Fig. 1.

Table 2.

3.3. Catalytic activity studies

3.3.1. Oxidation of benzyl alcohol

The catalytic activity of complex **1** was tested in the oxidation of alcohols (Scheme 2). The catalytic oxidation of benzyl alcohol as a representative substrate with hydrogen peroxide was studied in the presence of complex **1**. Aqueous hydrogen peroxide (30%) was selected as oxidant by considering its high selectivity, atom economy, and environmentally benign properties. The results of control experiments revealed that the presence of catalyst and oxidant (H₂O₂) is essential for the oxidation. To achieve the maximum oxidation of alcohols the effective parameters for suitable reaction conditions such as the oxidant concentration (moles of oxidant per moles of substrate), solvent, and temperature of the reaction were investigated. Results of the studies are summarized in Table 3. In all these reactions benzyl alcohol gave the benzaldehyde with

100% selectivity by catalyst and there was not any other product. The effect of oxidant concentration on the oxidation of alcohols by complex **1** is illustrated in Fig. 2. Different oxidant/substrate molar ratios (1:1, 2:1, 3:1 and 4:1) were considered while the ratio of benzyl alcohol (1.0 mmol) to catalyst (1.4 μ mol, 0.001 g) in 3 mL of acetonitrile was constant. The conversion of benzyl alcohol increased with increasing the amount of hydrogen peroxide in the reaction mixture. When H₂O₂/substrate molar ratio was 3:1, the maximum conversion of 76% was obtained at 60 \pm 1 $^{\circ}$ C. In order to find the effect of reaction atmosphere on catalytic activity of complex, this reaction was repeated in N₂ atmosphere. The result of this reaction was same with result of air atmosphere which indicates the atmospheric oxygen has not effect on catalytic reactivity of complex **1**.

In order to get the best reaction temperature, oxidation of alcohols was studied at 25 (room temperature), 40, 60, and 80 $^{\circ}$ C and the results are shown in Fig. 3. At room temperature the oxidation of benzyl alcohol was very low. Increasing the reaction temperature from 25 to 80 $^{\circ}$ C increased the conversion of benzyl alcohol and maximum conversion was obtained as 92% after 5 hours. Fig. 4 illustrates the influence of the solvent nature in the catalytic oxidation of benzyl alcohol. Acetonitrile, acetone, toluene, dichloromethane, chloroform, DMSO, THF and ethyl acetate were used as solvents. It was observed that the catalytic activity of the catalyst decreased with respect to acetonitrile > acetone > THF > dichloromethane > chloroform > toluene > ethyl acetate > DMSO. Overall, the reactivity of catalyst in other solvents was very much lower than in acetonitrile.

Scheme 2.

Fig. 2.

Fig. 3.

Table 3.

Fig. 4.

3.3.2. Oxidation of various primary alcohols

In order to explore further the oxidation potential of the complex **1**, oxidation of various primary alcohols was performed under the same reaction conditions which proved to be the best for benzyl alcohol. The effect of substituents and nature of aromatic rings on alcohol oxidation was studied. The results are shown in Table 4 and indicate this catalytic system led to the oxidation of different primary alcohols to corresponding aldehydes with 100% selectivity. It seems that efficiency of oxidation in this catalytic system is dependent on the electronic and steric demands of the substrate. It was observed that the presence of electron-donating (–OMe, –OH) group on the *para*-position of benzyl alcohol enhanced the conversion in comparison with molecule having no substituent on the ring (entries 1, 2 and 3). In addition, electron-withdrawing –Cl and especially –NO₂ groups on the phenyl ring decelerated the oxidation reaction (entries 4 and 5). The influence of steric factors in this catalytic system is also notable. The lower conversion of *ortho*-substituted alcohols such as 2-Cl- and 2-NO₂-benzyl alcohol (entries 7 and 8) in comparison with the corresponding non-hindered alcohols at similar reaction times may be related to the steric hindrance at vicinity of the active Cr center. It is to note that the oxidation of 2-hydroxy-benzyl alcohol is same with 4-hydroxy-benzyl alcohol (entries 2 and 6) and this may be due to formation of hydrogen bonds through phenolic O–H in *ortho* position respect to the alcoholic group of the substrate and this may help to approach the substrate near to the Cr-center.

Table 4.*3.3.2. Possible mechanism of the catalytic reaction*

It was observed that the mixed ligand complexes of Cr(III) generate Cr(V)=O intermediate with a variety of oxidants [19^{c-e},32]. Several studies have been reported that the oxido-chromium(V) complexes probably are intermediates in oxidation reactions of various organic substrates catalyzed by Cr(III) complexes [19^{c-e},32,33]. The Cr(V)=O species are capable intermediates for efficient oxidizing of organic substrates. The initial solution of this catalytic system is light green in color. When H₂O₂ was added to the solution, the color slowly changed to blue. This phenomenon expresses the interaction of peroxido group with Cr(III) center and the presence of strong charge transfer transition in new product. At higher temperatures this change is much faster than at room temperature. The observed change maybe is due to the generation of oxido-chromium(V) species.

In general the total mechanism of the reaction is not fully clear. However, on the basis of the changes in color of reaction mixture and reported mechanisms for oxidation reactions catalyzed by Cr(III) complexes [19^{c-e},32,33], it is predicted that the key step in this process is the oxidation of alcohols by oxido-chromium(V) species formed in the presence of hydrogen peroxide. The proposed catalytic pathway is shown in Scheme 3. A similar mechanism has been reported for the catalytic oxidation of benzyl alcohol with heterogenised Cr(III) complexes of salen ligands [34].

Scheme 3.**4. Conclusion**

A new chromium(III) complex of tetradentate bis(phenolate) ligand was synthesized and characterized by spectroscopic and single crystal X-ray analyses. The catalytic ability

of this complex was investigated by using the environmentally benign and clean oxidant H₂O₂ for oxidation of primary alcohols. The effects of various parameters including the molar ratio of the oxidant to substrate, the temperature, and the solvent have been studied and the optimized conditions were obtained. This complex is selective and active catalyst for oxidation of primary alcohols to corresponding aldehydes. The presence of electron-withdrawing and electron-donating groups on the phenyl ring of benzyl alcohol in the reactivity of catalysts was investigated. Excellent conversions were obtained for the oxidation of alcohols containing electron-donating groups on *para*-position.

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Appendix A. Supplementary material

CCDC 963747 contains the supplementary crystallographic data for **1**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Scheme/ Figures/ Tables caption

Scheme 1. Synthesis of a) bis(phenolate) ligand, H₂bp, and b) complex (**1**)

Scheme 2. Catalytic Oxidation of alcohols in the presence of Cr(III) complex

Scheme 3. Proposed mechanism for catalytic oxidation of alcohols using complex **1** in the presence of H₂O₂

Fig. 1. The X-ray structure of the complex molecule Cr(bp)(N₃)(CH₃OH) present in [Cr(bp)(N₃)(CH₃OH)]·2CH₃OH (**1**). The disorder in *t*-Bu and N₃⁻, as well as the solvent molecules are omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Not fully-occupied atoms are shown as spheres of arbitrary radii

Fig. 2. Effect of H₂O₂ concentration on the oxidation of benzyl alcohol by **1**. *Reaction conditions:* Catalyst, complex **1**, 1.40 μmol (0.001 g); CH₃CN, 3 mL; *n*-octane, 1.0 mmol; benzyl alcohol, 1 mmol; temperature, 60±1 °C

Fig. 3. Effect of the reaction temperature on the oxidation of benzyl alcohol by **1**. *Reaction conditions:* Catalyst, complex **1**, 1.40 μmol (0.001 g); CH₃CN, 3 mL; *n*-octane, 1.0 mmol; benzyl alcohol, 1 mmol; H₂O₂, 3 mmol

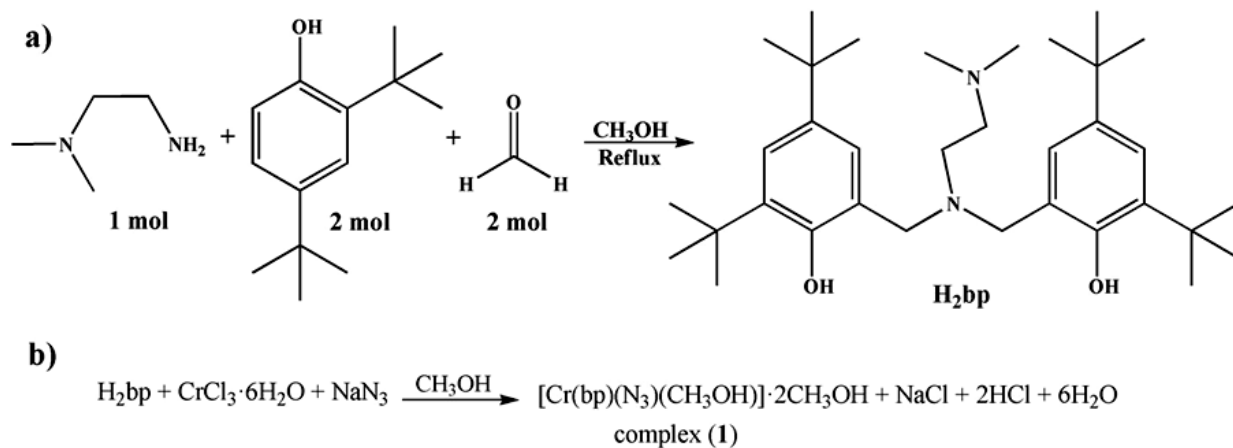
Fig. 4. Effects of the solvents on the oxidation of benzyl alcohol by **1**. *Reaction conditions:* Catalyst, complex **1**, 1.40 μmol (0.001 g); solvent, 3 mL; *n*-octane, 1.0 mmol; benzyl alcohol, 1 mmol; H₂O₂, 3 mmol; temperature, 80±1 °C

Table 1. Crystallographic data of **1**

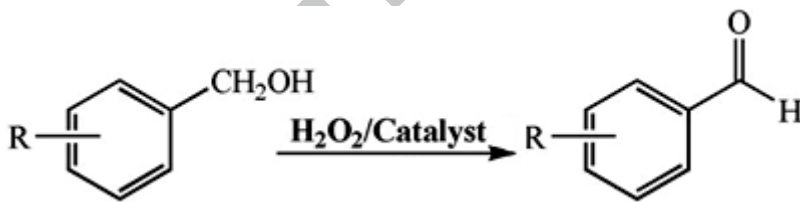
Table 2. Selected bond lengths (Å) and angles (°) in complex **1**

Table 3. Comparison the catalytic activities of catalysts **1** in the oxidation of benzyl alcohol with hydrogen peroxide in different conditions

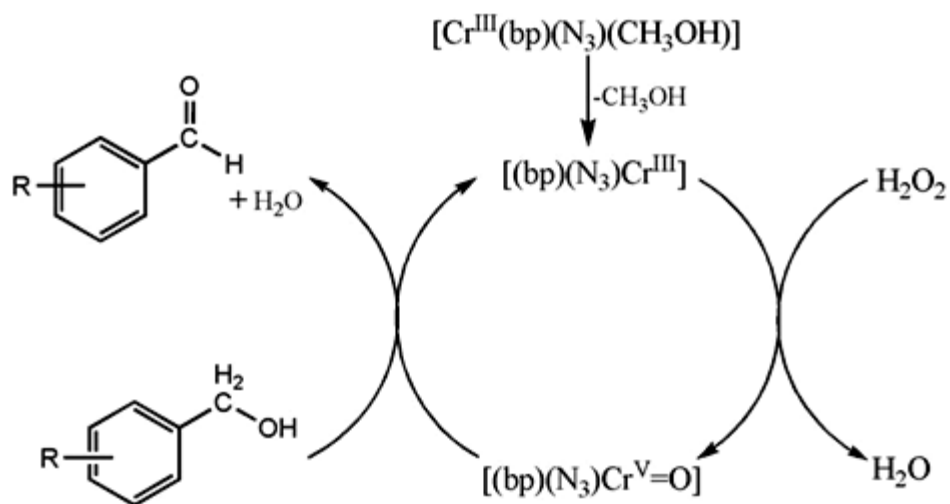
Table 4. Oxidation of various primary alcohols with complex **1**



Scheme 1.



Scheme 2.



Scheme 3.

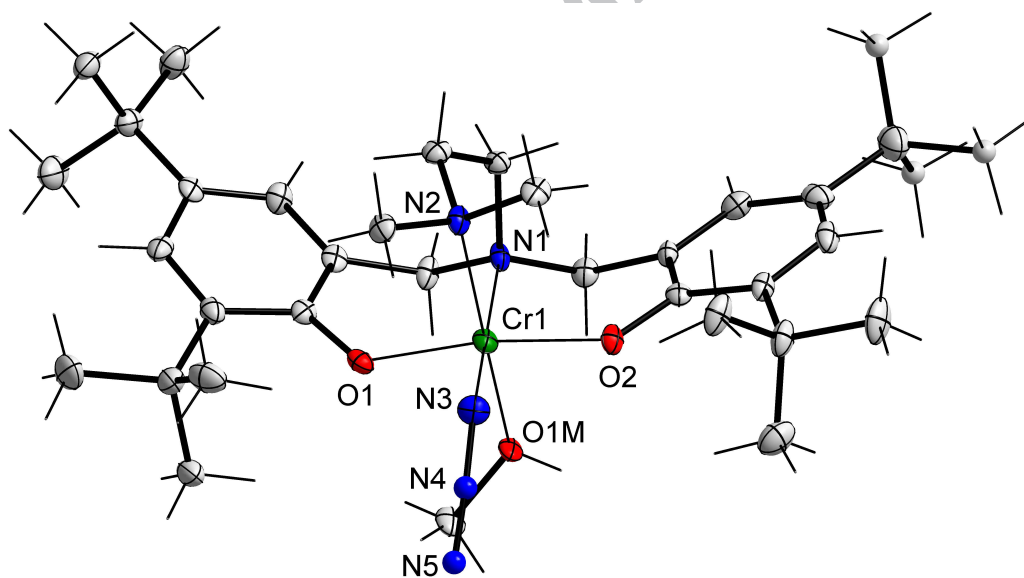


Fig. 1.

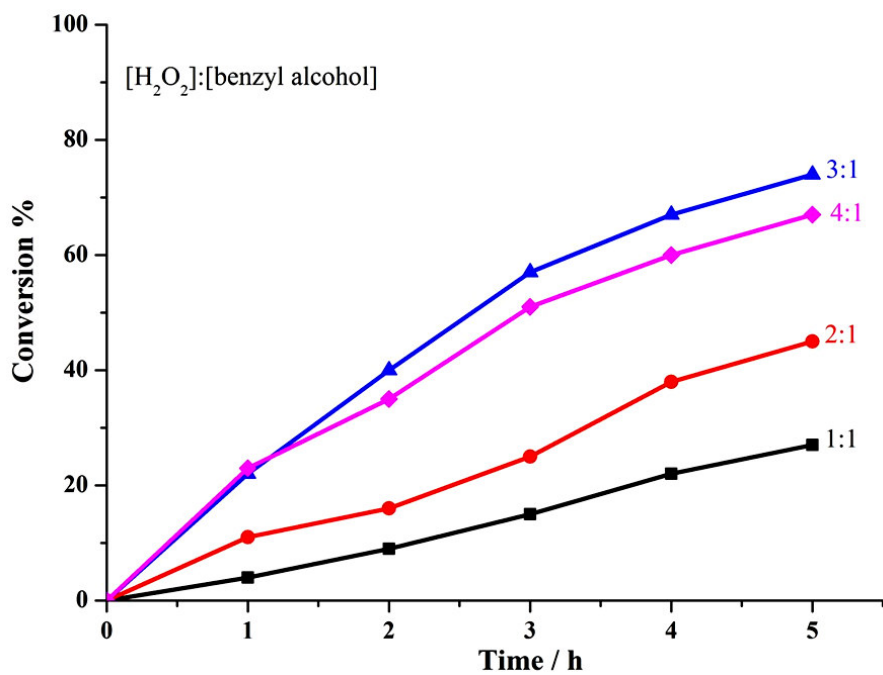


Fig. 2.

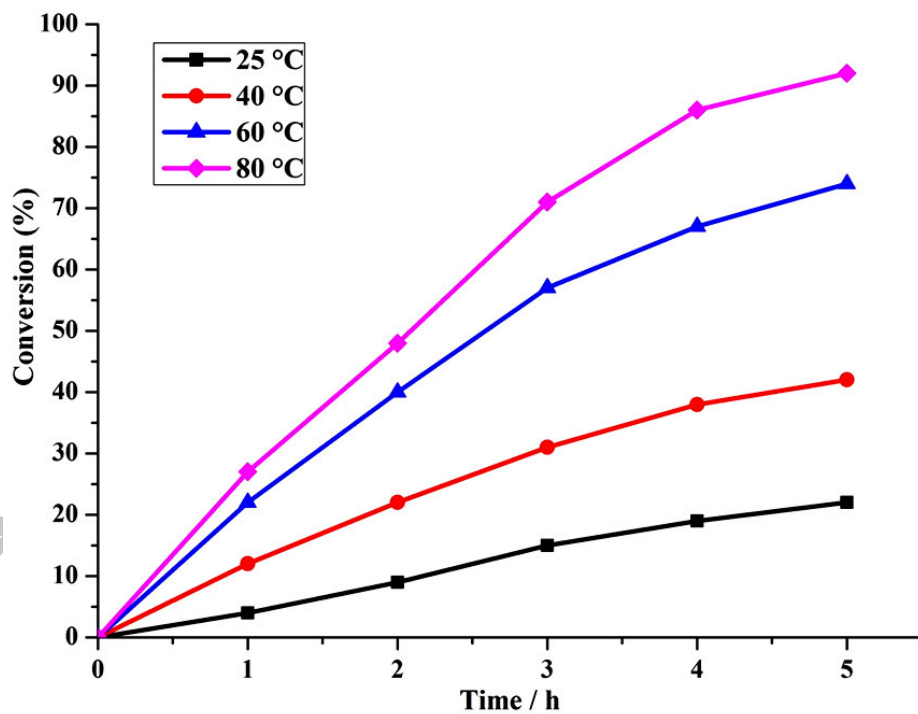


Fig. 3.

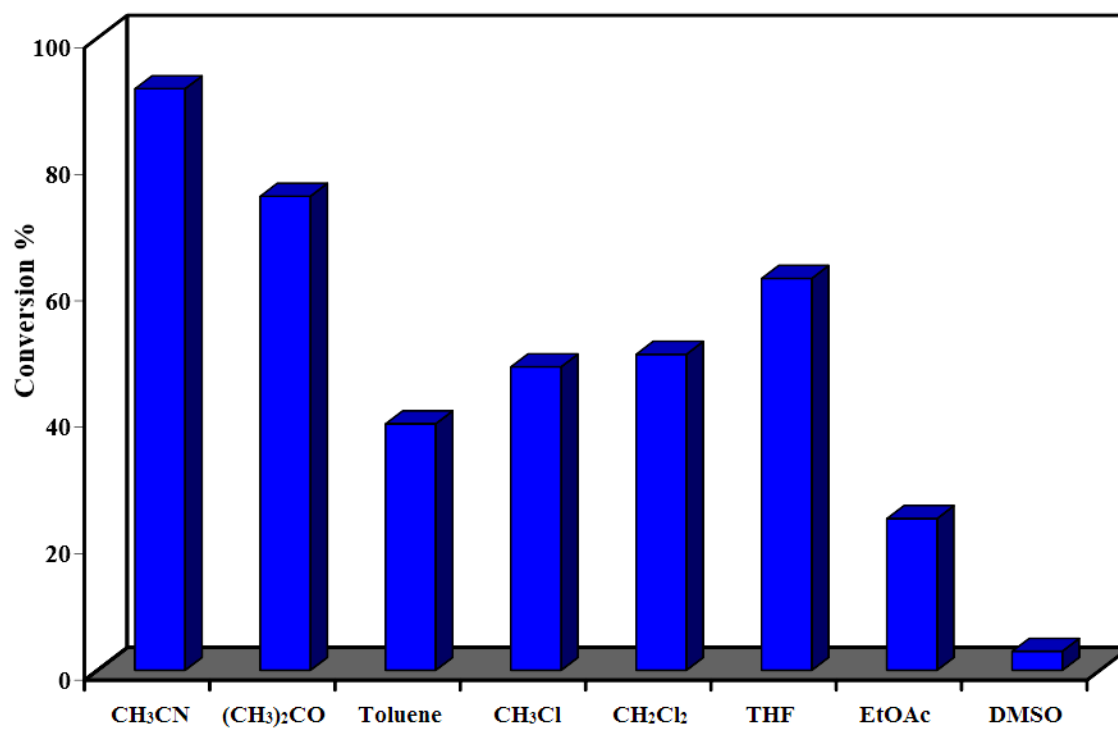


Fig. 4.

Table 1. Crystallographic data of **1**

CCDC No.	963747
Formula	C ₃₇ H ₆₆ CrN ₅ O ₅
M_r /g mol ⁻¹	712.94
Crystal size/mm	0.35 × 0.16 × 0.09
Crystal shape, color	Block, green
T /K	100(2)
Radiation	MoK α ($\lambda = 0.71073$ Å)
Crystal system, space group	Monoclinic, $C2/c$
a /Å	31.189(9)
b /Å	10.584(4)
c /Å	24.920(8)
β /°	103.04(3)
V /Å ³	8014(5)
Z	8
Calc. density/g cm ⁻³	1.182
$F(000)$	3096
μ /mm ⁻¹	0.33
Absorption correction	Empirical (multi-scan)
T_{\min}/T_{\max}	0.620/1.000
Measured reflections	16987
R_{int}	0.115
h, k, l	-38→29, -13→9, -30→30
Θ range	2.82–26.00
Independent reflections	7678
Observed reflections	3737
Data/Parameters/Restraints	7678/447/9
$R1(F_{\text{obs}})$	0.085 ^{a)}
$wR2(F^2)$	0.207 ^{a)}
GooF = S	1.00
Shift/error _{max}	0.000
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}/e$ Å ⁻³	0.62/-0.81

^{a)} $R1 = \sum \|F_o\| - |F_c| / \sum \|F_o\|$; $wR2 = \sqrt{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]}$; Detailed information on the weighting scheme (w) is given in the crystallographic information file (CIF).

Table 2. Selected bond lengths (Å) and angles (°) in complex **1**

Bond	Å	Angle	°
Cr1–O2	1.939(3)	O1–Cr1–O1M	86.71(14)
Cr1–O1	1.949(4)	N3–Cr1–O1M	94.26(17)
Cr1–N3	2.022(5)	O2–Cr1–N1	90.02(15)
Cr1–O1M	2.029(3)	O1–Cr1–N1	92.40(15)

Cr1–N1	2.081(4)	N3–Cr1–N1	172.98(17)
Cr1–N2	2.140(4)	O1M–Cr1–N1	92.33(15)
N3–N4	1.207(6)	O2–Cr1–N2	95.95(15)
N4–N5	1.162(7)	O1–Cr1–N2	92.98(15)
Angle	°	N3–Cr1–N2	90.52(17)
O1–Cr1–O2	170.97(14)	O1M–Cr1–N2	175.21(17)
O2–Cr1–N3	88.23(16)	N1–Cr1–N2	82.90(16)
O1–Cr1–N3	90.36(17)	N4–N3–Cr1	134.0(5)
O2–Cr1–O1M	84.50(14)	N3–N4–N5	177.3(12)

Table 3. Comparison the catalytic activities of catalysts **1** in the oxidation of benzyl alcohol with hydrogen peroxide in different conditions

Entry	Catalyst	H ₂ O ₂ (mmol)	Solvent	Temp.	Yield (°C) ^a	Selectivity (%)	TOF(h ⁻¹)
1	1	1	CH ₃ CN	60	27	100	39
2	1	2	CH ₃ CN	60	45	100	64
3	1	3	CH ₃ CN	60	76	100	109
4	1	4	CH ₃ CN	60	67	100	96
5	1	3	CH ₃ CN	25	22	100	31
6	1	3	CH ₃ CN	40	42	100	60
7	1	3	CH ₃ CN	80	92	100	131
8	1	3	(CH ₃) ₂ CO	80	75	100	107
9	1	3	Toluene	80	39	100	56
10	1	3	CHCl ₃	80	48	100	67
11	1	3	CH ₂ Cl ₂	80	50	100	71
12	1	3	THF	80	62	100	89
13	1	3	EtOAc	80	24	100	34
14	1	3	DMSO	80	3	100	4

Reaction conditions: catalyst, 1.40 μmol; benzyl alcohol, 1 mmol; *n*-octane, 1.0 mmol; solvent, 3 mL; time, 5 hours

^a Yields are based on the starting benzyl alcohol

Table 4. Oxidation of various primary alcohols with complex **1**

Entry	Substrate	Product	Yield (Selectivity)	TON (TOF/h ⁻¹)
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ACCEPTED MANUSCRIPT

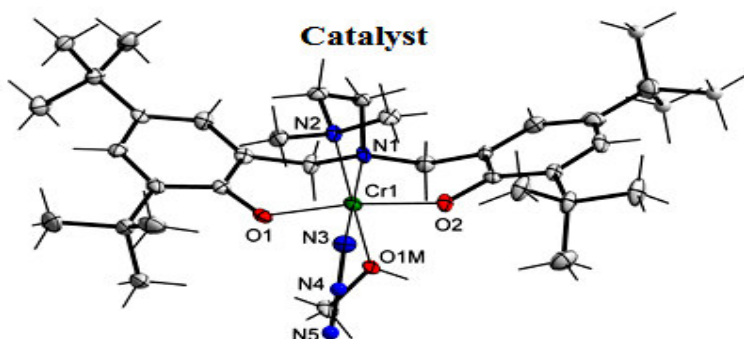
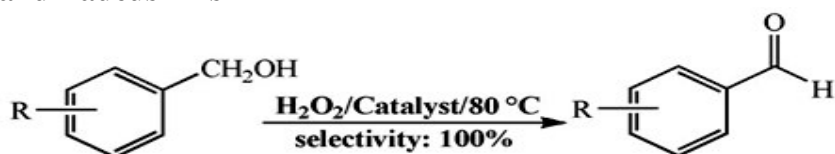
1			98 (100)	700(140)
2			96 (100)	686 (137)
3			92 (100)	657 (131)
4			90 (100)	643 (129)
5			86 (100)	614 (123)
6			96 (100)	686 (137)
7			85 (100)	607 (121)
8			76 (100)	543 (109)

Reaction conditions: catalyst, 1.40 μmol ; substrate, 1 mmol; H_2O_2 , 3 mmol; *n*-octane, 1.0 mmol; solvent, CH_3CN , 3 mL; time, 5 h, temperature, 80 ± 1 $^\circ\text{C}$

Graphical abstract

Synthesis, characterization and catalytic activity of new Cr(III) complex in oxidation of primary alcohols to aldehydes

Nader Noshiranzadeh,^{a,34} Rahman Bikas,^a Katarzyna Ślepokura,^b Mina Mayeli,^a and Tadeusz Lis^b



Graphical abstract

Synthesis, characterization and catalytic activity of new Cr(III) complex in oxidation of primary alcohols to aldehydes

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- ✓ New method for oxidation of primary alcohols to corresponding aldehydes
- ✓ Synthesis and structure of a new Cr(III) complex with bis(phenolate) ligand
- ✓ Catalytic behavior of the Cr(III) complex in oxidation of primary alcohols
- ✓ The effects of various parameters in oxidation of primary alcohols were studied
- ✓ Excellent conversions were obtained for benzyl alcohols containing electron-donating groups