Tris-chelate complexes of cobalt(III) with N-[di(alkyl/aryl)carbamothioyl] benzamide derivatives: Synthesis, crystallography and catalytic activity in TBHP oxidation of alcohols

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A B S T R A C T

New six coordinated *tris*-chelate cobalt(III) complexes of the type $[Co(L)_3]$ (**1–4**) {where HL = N-[di(alkyl/aryl)carbamothioyl]benzamide derivatives}were prepared from the reaction between $CoCl_2 \cdot 6H_2O$ and N-[di(alkyl/aryl)carbamothioyl]benzamide in ethanol and characterized by elemental analysis and spectral data (UV/Vis, IR, ^{1}H & ^{13}C NMR). The molecular structure of a representative complex $[Co(L1)_3]$ (**1**) [where HL1 = N-(diisopropylcarbamothioyl)benzamide], was determined by single crystal X-ray diffraction method and reveals a distorted octahedral geometry and a facial configuration of S atoms around the Co(III) center. These complexes act as efficient catalysts for the oxidation of alcohols to their corresponding aldehydes or ketones in presence of *tert*-butyl hydroperoxide (TBHP) at 80 °C.

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1. Introduction

Selective oxidation of alcohols to the corresponding carbonyl compounds plays an important role in organic synthesis and in the fine chemicals industry, often being a key step for the preparation of important synthons or directly affording fine chemicals and valuable specialty products such as fragrances, drugs, vitamins and hormones [1–3]. The stoichiometric amounts of hazardous inorganic oxidants, notably Cr(VI)/Mn(IV), used in these conversions generate copious amounts of waste [4]. In terms of economical benefit and environmental impact, catalytic oxidation processes are extremely valuable. In recent years, there has been a growing interest in the search for new transition metal catalytic systems for the oxidation of alcohols that use hydrogen peroxide [5,6], *tert*-butyl hydroperoxide (TBHP) [7] or dioxygen [8–14] as the ultimate stoichiometric oxidant, due to their obvious economic and ecological advantages.

Cobalt(II) salts and complexes have been used as homogeneous catalysts in the oxidation of alcohols to the corresponding carbonyl compounds. Cobalt(III)-peroxo/alkylperoxo species are considered as intermediates in these catalytic processes [15–18]. Thus, the direct use of Co(III) may enhance the rate of reactions and hence be beneficial. In addition, the use of Co(III) complexes stabilized by suitable ligand environments leads to a greater catalyst stability owing to the relative substitutional inertness of Co(III) [19]. With this in mind, several Co(III) catalytic systems including $[Co(acac)_3]$ [20,21], Co(III)-oxo cubanes [22,23] and *o*-phenylenebis(N′-methyloxamidate) cobalt(III) complexes [24,25] have been developed.

N-[Di(alkyl/aryl)carbamothioyl]benzamide derivatives are versatile class of ligands which can form stable complexes with a large number of transition metals. In general, N-[di(alkyl/aryl)carbamothioyl]benzamide derivatives are known to coordinate in different ways [26]. The enormous increase in the attention paid to these complexes has been mainly driven by their applications in precious metal separation and extraction [26,27], single source precursors for nanomaterials [28], biological activity [29–33], etc. Though these complexes have been used in various fields, their application in catalysis is comparitively unexplored. We have utilized N-[di(alkyl/aryl)carbamothioyl]benzamide complexes of Ru(II) [34], Ru(III) [35] and Cu(I) [36] as catalysts for the oxidation of alcohols to the corresponding carbonyl compounds in the presence of N-methylmorpholine-N-oxide (NMO)/hydrogen peroxide as oxidant. All these catalytic reactions are effective

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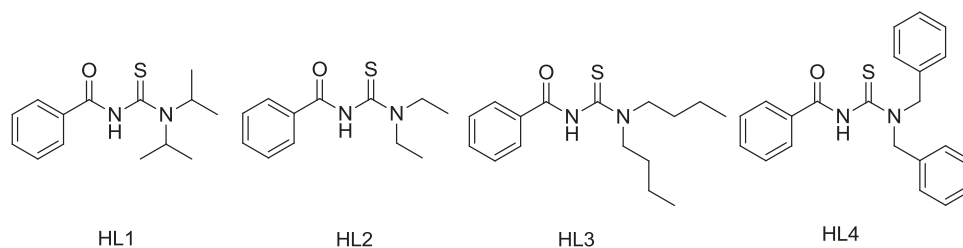 *E-mail address:* kar@nitt.edu (R. Karvembu).

Fig. 1. Structures of ligands employed in this study.

in terms of the yield of products and proceeded under mild reaction conditions. In continuation of our ongoing research on the catalytic applications of transition metal complexes of *N*-[di(alkyl/aryl)carbamothioyl]benzamide derivatives, we report herein the synthesis, the crystal structure and the catalytic activity of their *tris*-chelate Co(III) complexes. While some Co(III) complexes with *N*-[di(alkyl/aryl)carbamothioyl]benzamide derivatives are known [37–39], this report is the first describing their catalytic applications. The structures of the ligands used in this work are shown in Fig. 1.

2. Experimental

2.1. Materials and reagents

All the chemicals were obtained from commercial sources and used as received. The solvents were purified and dried in accordance with the standard literature methods. The precursor [CoCl$_2$(PPh$_3$)$_2$] was prepared by the literature procedure [40] while CoCl$_2$·6H$_2$O was purchased from Loba Chemie (India). The ligands HL1, HL2, HL3 and HL4 were prepared from benzoyl chloride, potassium thiocyanate and the corresponding secondary amine in dry acetone [41].

2.2. Physical measurements

Microanalysis was carried out with a Vario EL AMX-400 elemental analyzer. Melting points were recorded with a Veego VMP-D melting point apparatus and were uncorrected. FT-IR spectra were recorded as KBr pellets with a PerkinElmer Spectrum RX1 FT-IR spectrophotometer in the range 4000–400 cm^{-1}. Electronic spectra of the complexes were recorded in ethanol solutions using a PG Instruments Ltd T90+ spectrophotometer in the 800–200 nm range. Magnetic susceptibility measurements were made with a Sherwood Scientific auto magnetic susceptibility balance. ^{1}H and ^{13}C NMR spectra were recorded in Bruker Avance 400 MHz instrument in acetone-d$_6$. TMS was used as an internal standard for ^{1}H and ^{13}C NMR spectra. The capillary gas chromatography was performed on a Shimadzu GC-2010 gas chromatograph with a RTX-5 column (60 m length, 0.32 mm inner diameter).

2.3. Preparation of Co(III) complexes

All the complexes were prepared using the following general procedure. CoCl$_2$·6H$_2$O (100 mg, 0.42 mmol) in ethanol (8 mL) was added dropwise to ligand (HL) (296.4–454.2 mg, 1.26 mmol) dissolved in ethanol (8 mL) in the presence of a few drops of Et$_3$N with a constant stirring for 30 min. The precipitate formed was filtered, washed with a small amount cold ethanol and dried *in vacuo*.

[Co(L1)$_3$] (**1**) was prepared from CoCl$_2$·6H$_2$O (100 mg, 0.42 mmol) and HL1 (330.5 mg, 1.26 mmol). Yield: 88%, decomposition point: 180 °C, ^{1}H NMR (acetone-d$_6$): δ = 7.36–8.23 (m, 15H, aromatic), 3.86 (br s, 6H, CH), 1.60 (d, *J* = 8 Hz, 18H, CH$_3$), 1.29 (d, *J* = 8 Hz, 18H, CH$_3$) ppm. ^{13}C NMR (acetone-d$_6$): δ = 175.66, 173.97 (C=S), 139.57, 139.08 (C=O), 130.90, 129.12, 127.67 (aromatic), 51.95, 49.31 (CH), 20.92, 20.35, 19.23, 19.03 (CH$_3$) ppm. FT-IR (KBr, cm^{-1}): ν(N–H) absent; ν(C=O) 1476; ν(C=S) 1201. UV [Ethanol, λ in nm (log ε)]: 206 (4.58), 281 (4.68), 373 (3.83). Anal. Calcd. for C$_{42}$H$_{57}$CoN$_6$O$_3$S$_3$ (%): C, 59.40; H, 6.94; N, 9.89; S, 11.32. Found (%): C, 59.35; H, 6.88; N, 9.82; S, 11.30.

[Co(L2)$_3$] (**2**) was prepared from CoCl$_2$·6H$_2$O (100 mg, 0.42 mmol) and HL2 (296.4 mg, 1.26 mmol). Yield: 85%, decomposition point: 175 °C, ^{1}H NMR (acetone-d$_6$): δ = 7.28–8.15 (m, 15H, aromatic), 3.83 (m, 12H, CH$_2$), 1.20 (t, 9H, CH$_3$), 0.82 (t, 9H, CH$_3$) ppm. ^{13}C NMR (acetone-d$_6$): δ = 174.64, 173.78 (C=S), 137.98 (C=O), 130.33, 128.39, 126.92 (aromatic), 50.11, 50.01 (CH$_2$), 12.68, 12.50 (CH$_3$) ppm. FT-IR (KBr, cm^{-1}): ν(N–H) absent; ν(C=O) 1486; ν(C=S) 1209. UV [Ethanol, λ in nm (log ε)]: 206 (4.49), 280 (4.41), 371 (3.73). Anal. Calcd. for C$_{36}$H$_{45}$CoN$_6$O$_3$S$_3$ (%): C, 56.52; H, 5.92; N, 10.98; S, 12.57. Found (%): C, 56.42; H, 5.85; N, 10.89; S, 12.49.

[Co(L3)$_3$] (**3**) was prepared from CoCl$_2$·6H$_2$O (100 mg, 0.42 mmol) and HL3 (368.4 mg, 1.26 mmol). Yield: 80%, decomposition point: 225 °C, ^{1}H NMR (acetone-d$_6$): δ = 7.34–8.21 (m, 15H, aromatic), 3.86 (m, 12H, CH$_2$), 1.70 (m, 12H, CH$_2$), 1.37 (m, 12H, CH$_2$), 0.92 (m, 18H, CH$_3$) ppm. ^{13}C NMR (acetone-d$_6$): δ = 175.31, 174.45 (C=S), 138.65 (C=O), 131.01, 129.24, 129.05, 127.58 (aromatic), 50.79, 50.69, 26.10, 19.99, 19.87 (CH$_2$), 13.36, 13.18 (CH$_3$) ppm. FT-IR (KBr, cm^{-1}): ν(N–H) absent; ν(C=O) 1491; ν(C=S) 1208. UV [Ethanol, λ in nm (log ε)]: 208 (4.83), 282 (4.92), 376 (4.03). Anal. Calcd. for C$_{48}$H$_{69}$CoN$_6$O$_3$S$_3$ (%): C, 61.77; H, 7.44; N, 9.00; S, 10.30. Found (%): C, 61.70; H, 7.34; N, 8.95; S, 10.20.

[Co(L4)$_3$] (**4**) was prepared from CoCl$_2$·6H$_2$O (100 mg, 0.42 mmol) and HL4 (454.2 mg, 1.26 mmol). Yield: 90%, decomposition point: 105 °C, ^{1}H NMR (acetone-d$_6$): δ = 7.15–8.28 (m, 45H, aromatic), 5.21 (m, 12H, CH$_2$) ppm. ^{13}C NMR (acetone-d$_6$): δ = 177.24, 175.93 (C=S), 138.65, 136.85, 136.09 (C=O), 131.59, 129.35, 128.51, 127.91, 127.53, 127.37, 127.14 (aromatic), 52.70, 51.83 (CH$_2$) ppm. FT-IR (KBr, cm^{-1}): ν(N–H) absent; ν(C=O) 1494; ν(C=S) 1206. UV [Ethanol, λ in nm (log ε)]: 206 (4.36), 284 (4.34), 375 (3.48). Anal. Calcd. for C$_{66}$H$_{57}$CoN$_6$O$_3$S$_3$ (%): C, 69.69; H, 5.04; N, 7.38; S, 8.45. Found (%):C, 69.60; H, 5.01; N, 7.33; S, 8.38.

2.4. X-ray structure determination

Green crystals of [Co(L1)$_3$] (**1**) were grown at room temperature from a ethanol and dichloromethane mixture (1:3) by the diffusion of diethyl ether vapour, and a plate having dimensions 0.05 mm × 0.20 mm × 0.25 mm was selected for the study. Data were collected at 100(2) K on an Agilent Technologies SuperNova Dual diffractometer with an Atlas detector using Mo-K$_\alpha$ radiation so that θ_{max} = 27.5°. The data set was reduced and corrected for absorption effects using CrysAlis PRO [42]. The structure was solved by direct-methods with SHELXS-97 [43] and refinement (anisotropic displacement parameters, hydrogen atoms in the riding model approximation and a weighting scheme of the form $w = 1/[\sigma^2(F_o{}^2) + (0.030P)^2 + 0.841P]$ for $P = (F_o{}^2 + 2F_c{}^2)/3$) was on F^2 by means of SHELXL-97 [43]. The crystallographic data and the final refinement details are given in Table 1. Figs. 2 and 3 were

Table 1
Crystallographic details for **1**.

Formula	$C_{42}H_{57}CoN_6O_3S_3$
Molecular weight	849.05
T/K	100(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	11.0327(4)
b (Å)	13.7430(6)
c (Å)	16.0505(7)
α (°)	100.662(4)
β (°)	93.721(3)
γ (°)	112.628(4)
V (Å^3)	2182.52(16)
Z	2
D_{calc} (Mg m^{-3})	1.292
No. reflections measured	18,005
No. unique reflections	9632
No. observed reflections [$I > 2\sigma(I)$]	7173
R_1 [$I > 2\sigma(I)$]	0.048
wR_2 (all data)	0.104
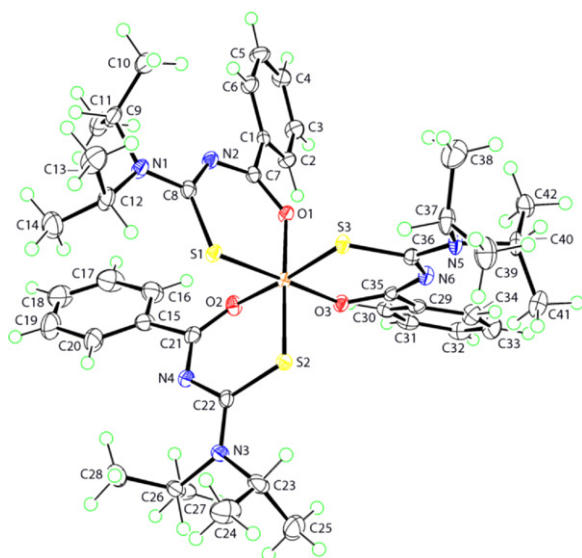
Fig. 2. Molecular structure of [Co(L1)$_3$] (**1**) showing the atom numbering scheme and displacement ellipsoids at the 50% probability level.
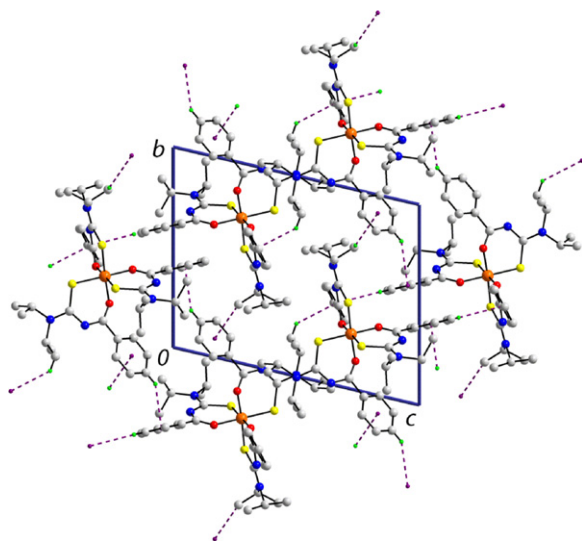
Fig. 3. View of the unit cell contents of [Co(L1)$_3$] (**1**) shown in projection down the *a*-axis. The dashed lines represent C–H…π interactions. Hydrogen atoms not involved in C–H…π interactions have been omitted for reasons of clarity.
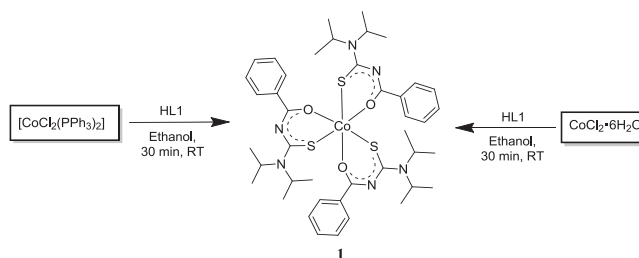
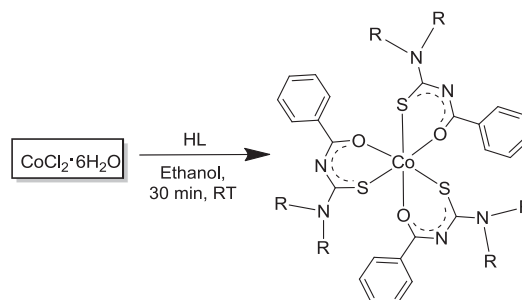**Scheme 1.** Synthesis of [Co(L1)$_3$] (**1**).

drawn with ORTEP [44], at the 50% probability level, and DIAMOND [45], arbitrary spheres, respectively. The data manipulation and the interpretation were done with WinGX [46] and PLATON [47].

2.5. Procedure for catalytic oxidation

To a solution of alcohol (1 mmol) in acetonitrile solvent (10 mL), *tert*-butyl hydroperoxide (287 μL, 3 mmol) and the complex **4** (7 mg, 0.01 mmol) were added. The solution was stirred at 80 °C for 24–48 h. At the requisite time, aliquots of the reaction mixture were removed and the alcohol and aldehyde/ketone were extracted with n-hexane. The n-hexane extract was then analyzed by GC. Authentic samples were used to identify the reaction products and determine their percentage yields by comparison of retention times and corresponding peak areas under identical experimental conditions. The area normalization method was employed to calculate the percentage yields of the formed products.

3. Results and discussion

The reaction between [CoCl$_2$(PPh$_3$)$_2$] and HL1 in 1:2 stoichiometry was carried out in ethanol in the presence of a few drops of triethyl amine in order to prepare a complex with the formula [Co(L1)$_2$(PPh$_3$)$_2$] but the analytical, spectral and crystallographic data indicated the formation of [Co(L1)$_3$] (Scheme 1). Reactions were also conducted changing solvents as well as the molar ratios of ligands in order to obtain the desired cobalt phosphine complex, but in all the cases only [Co(L1)$_3$] was obtained. The complex [Co(L1)$_3$] was also obtained by the reaction of CoCl$_2$·6H$_2$O with HL1 (molar ratio of CoCl$_2$·6H$_2$O:HL1 = 1:3) in ethanol in the presence of triethyl amine (Scheme 1). Subsequently, CoCl$_2$·6H$_2$O was used as the cobalt precursor for the preparation of complexes with HL2, HL3 and HL4 (Scheme 2). The oxidation of cobalt(II) by air (dissolved in solution) occurred during the synthesis. The Co(III) complexes were isolated as green or brown solids and these were highly soluble in acetone, acetontrile, DMSO, DMF, partially soluble in ethanol, methanol, chloroform and dichloromethane and insoluble in n-hexane. All the complexes are air-stable and hence are suitable for catalytic oxidation reactions. The analytical data

R= CH(CH$_3$)$_2$ (HL1), CH$_2$CH$_3$ (HL2), CH$_2$CH$_2$CH$_2$CH$_3$ (HL3) or CH$_2$C$_6$H$_5$ (HL4).

Scheme 2. Synthesis of Co(III) complexes.

obtained are in excellent agreement with the proposed molecular formulae.

3.1. Spectroscopy

A very strong absorption band was observed around 3200 cm^{-1} in the FT-IR spectra of the free ligands which is characteristic of the N–H group [41]. This band disappeared in the spectra of **1–4** suggesting the deprotonation of the N–H group during the complex formation. In the FT-IR spectra of free carbamothioyl ligands, a strong band in the region 1652–1690 cm^{-1} and a medium intensity band in the region 1243–1314 cm^{-1} are attributed to C=O and C=S groups, respectively. In the FT-IR spectra of the complexes, these bands were observed in the lower frequency regions, i.e. 1476–1494 and 1201–1209 cm^{-1}, respectively, consistent with the reduced electron density in these bonds and therefore, suggesting the coordination of the O and S atoms to cobalt [37].

The new cobalt complexes were diamagnetic ($\mu_{eff} = 0$), indicating the presence of cobalt in the 3+ oxidation state. The electronic spectra in ethanol solution showed three bands/shoulders with absorption maxima values in the ranges of 206–208, 280–284 and 371–376 nm. High energy bands appeared in the regions 206–208 and 280–284 nm have been assigned to π–π^* transitions and a shoulder appeared in the region 371–376 nm have been attributed to charge transfer transition (LMCT) [48]. The UV–visible spectral data of complexes **1–4** are analogues to the results described earlier for facial *tris*-chelate Co(III) complexes [49].

The ^{1}H NMR spectra of complexes **1–4** in acetone-d$_6$ solution showed a complex multiplet around 7.15–8.28 ppm, which has been attributed to the aromatic protons present in the [*N*-di(alkyl/aryl)carbamothioyl]benzamide ligand. The characteristic N–H signal in the region 10.40–10.93 ppm in the ligands was not present in the ^{1}H NMR spectra of any of the complexes indicating deprotonation of N–H proton of the ligands upon coordination [50]. In addition, complex **1** showed two doublets at 1.29 and 1.60 ppm and a broad singlet at 3.68 ppm which have been assigned to methyl and methine protons of the ligand, indicating the methyl groups are in distinct magnetic environments. Complex **2** exhibited a multiplet around 3.83 ppm corresponding to the methylene protons and two triplets at 0.82 and 1.20 ppm corresponding to methyl protons, again indicating distinct environments for these groups. A multiplet was appeared around 3.86 ppm in complex **3** due to the methylene protons proximate to nitrogen. Complex **3** also exhibited two multiplets at 1.70 ppm and 1.37 ppm which are attributed to the remaining methylene protons of aliphatic carbon chain. A multiplet (merging of two triplets) around 0.92 ppm in complex **3** has been assigned to the methyl protons. Complex **4** showed a multiplet around 5.21 ppm corresponding to the methylene protons. ^{13}C NMR spectra of all the complexes (**1–4**) have been recorded in acetone-d$_6$ solution. The ^{13}C NMR spectra of the complexes showed the expected resonances. The signals observed in the range 126.92–131.59 ppm for all complexes have been assigned to the aromatic carbons of *N*-[di(alkyl/aryl)carbamothioyl]benzamide ligand. The resonances due to the C=S and C=O carbon nuclei in the Co(III) complexes have been shifted significantly with respect to the free ligands, and appeared in the regions of 173.78–177.24 ppm and 136.09–139.57 ppm, respectively, indicating the coordination of the ligands to cobalt through the S and O atoms [37]. All complexes exhibited resonances due to aliphatic carbons in the expected regions.

3.2. Crystal and molecular structure of *1*

The molecular structure of a representative complex, namely [Co(L1)$_3$] (**1**), was established by X-ray crystallography and is illustrated in Fig. 2. The Co center is *tris* chelated by three L1 anions,

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

Co–S(1)	2.2050(6)	Co–O(1)	1.9087(18)
Co–S(2)	2.2161(8)	Co–O(2)	1.9320(17)
Co–S(3)	2.2012(7)	Co–O(3)	1.9174(15)
C(8)–S(1)	1.744(3)	C(7)–O(1)	1.262(3)
C(22)–S(2)	1.741(2)	C(21)–O(2)	1.268(3)
C(36)–S(3)	1.740(2)	C(35)–O(3)	1.263(3)
S(1)–Co–O(3)	178.30(5)	S(2)–Co–O(1)	177.18(5)
S(3)–Co–O(2)	176.44(6)	S(1)–Co–S(2)	87.47(3)
S(1)–Co–S(3)	87.27(2)	S(2)–Co–S(3)	89.75(3)
O(1)–Co–O(2)	85.59(7)	O(1)–Co–O(3)	84.86(7)
O(3)–Co–O(2)	86.98(7)		

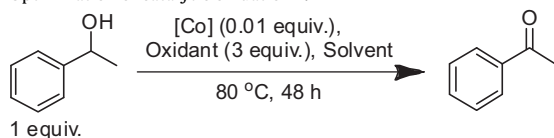each of which coordinates in the bidentate S,O mode. Within the octahedral geometry defined by the O$_3$S$_3$ donor set, the S atoms have a facial arrangement, and the three O atoms define an octahedral face. The ranges of Co–S and Co–O bond distances, Table 2, are each narrow. In terms of angles, the deviations from the ideal octahedral geometry are small with the *cis* angles ranging from 84.86(7)° to 93.45(6)°. The S–Co–S angles are systematically wider than the O–Co–O angles as expected on size considerations, Table 2. The three phenyl rings lie to the one side of the plane defined by the three O atoms whereas the *i*-Pr groups lie to the other side. This is consistent with the NMR study that indicated the inequivalent of the N-bound substituents in these non-labile Co(III) complexes. The crystal structure of the HL1 ligand is known [51] and available for comparison with the anions in **1**. There are two independent molecules in this structure and the C=S bond distances of 1.6687(15) and 1.6689(15) Å in these are significantly shorter than the C–S distances observed in (**1**), Table 2, consistent with the spectroscopic study. A similar observation pertains to the C=O bond distances of 1.2304(18) and 1.2343(18) Å. The overall coordination geometry observed in **1** is consistent with those seen in related structures reported in the literature [37,39,52].

There are a number intramolecular C–H...S and C–H...N interactions within the complex molecule of **1** which preclude the S1 and S2, and N2, N4 and N6 atoms from forming significant intermolecular contacts. The most notable intermolecular interactions operating in the crystal structure of **1** are of the type C–H...π [53]. These involve each of the phenyl rings and lead to a three-dimensional architecture, Fig. 3.

3.3. Catalytic oxidation

The new Co(III) complexes (**1–4**) have been used as catalysts for the oxidation of 1-phenylethanol (Table 3, entries 1–4) in acetonitrile solvent with TBHP at 80 °C. Though all the complexes exhibited good catalytic activity, complex **4** was chosen for optimizing the reaction conditions and extending the scope of substrates since yield of acetophenone (93%) was slightly higher (Table 3, entry 4). Generally, oxidation of alcohols catalyzed by Ru(II) [34], Ru(III) [35] and Cu(I) [36] complexes containing *N*-[di(alkyl/aryl)carbamothioyl]benzamide derivatives and triphenylphosphine was completed at room temperature with in 12 h. But in the present catalytic system with Co(III) complexes containing only *N*-[di(alkyl/aryl)carbamothioyl]benzamide derivatives, the reaction proceeded only at elevated temperature and requires 48 h; this may be due to the fact that *tris*-chelate Co(III) complex provides a coordination site for the formation of possible active species [Co(III)-peroxo] by dangling one of the coordinated *N*-[di(alkyl/aryl)carbamothioyl]benzamide ligands which normally requires high temperature and more time [54]. With complex **4** as catalyst, catalytic oxidation of 1-phenylethanol (Fig. 4) was carried out in different solvents (CH$_3$CN, (CH$_3$)$_2$CO, CH$_2$Cl$_2$, CH$_3$OH, C$_6$H$_6$ and DMF). When CH$_3$CN was used, a significant increase in the yield of acetophenone was observed. The catalytic oxidation of

Table 3
Optimization of catalytic oxidation[a].

$$\text{1-phenylethanol (OH)} \xrightarrow[\text{80 °C, 48 h}]{\substack{\text{[Co] (0.01 equiv.),} \\ \text{Oxidant (3 equiv.), Solvent}}} \text{acetophenone (O)}$$

1 equiv.

Entry	Catalyst	Solvent	Oxidant	Yield (%)[b]
1	**1**	CH_3CN	*t*-BuOOH	91
2	**2**	CH_3CN	*t*-BuOOH	92
3	**3**	CH_3CN	*t*-BuOOH	92
4	**4**	CH_3CN	*t*-BuOOH	93
5	**4**	CH_3CN	NMO	No reaction
6	**4**	CH_3CN	H_2O_2	No reaction
7	**4**	CH_3CN	H_5IO_6	50
8	**4**	CH_3CN	*t*-BuOOH	93[c]

[a] Reaction conditions: 1-phenylethanol (1 mmol), oxidant (3 mmol), catalyst (0.01 mmol),. solvent (10 mL), 80 °C, 48 h.

[b] Yield is determined by GC with area normalization; GC conditions: RTX-5 column, 60 m × 0.32 mm, 240 °C; FID detector, 270 °C; injector, 220 °C; carrier gas, N_2; rate: 1 mL/min.

[c] Reaction conditions: 1-phenylethanol (1 mmol), oxidant (3 mmol), catalyst (0.01 mmol), solvent (10 mL), 80 °C, 48 h, under nitrogen atmosphere.

1-phenylethanol (Table 3, entries 4–7) was studied with the different oxidants such as *tert*-butyl hydroperoxide, *N*-methylmorpholine-*N*-oxide, hydrogen peroxide and periodic acid with **4** as catalyst and CH_3CN as solvent. The oxidation of 1-phenylethanol did not proceed at all when NMO or H_2O_2 was used as an oxidant. When H_5IO_6 was used as the oxidant, the yield of acetophenone was found to be only 50%. Among these four oxidants, TBHP was found to be the best as it gave acetophenone in 93% yield. Hence, CH_3CN as solvent and TBHP as oxidant were used while extending the scope of substrates. It is further noted that 0.01 mmol of the Co(III) complex and 3 mmol of oxidant were sufficient for effective oxidation process. The control experiments were carried out under identical conditions with $CoCl_2 \cdot 6H_2O$ or HL4 as catalyst in the place of complex **4**. No oxidation was observed in these reactions. The oxidation of 1-phenylethanol (Table 3, entry 8) with complex **4** under nitrogen atmosphere also gave 93% of acetophenone, which indicates that only *tert*-butyl hydroperoxide acts as oxidant in these reactions and not air.

Having established the optimal conditions with 1-phenylethanol, the attention was switched to other substrates. The results of the oxidation of various alcohols in CH_3CN solvent using **4** as catalyst and TBHP as oxidant at 80 °C are shown in Table 4. Benzylic secondary alcohols (Table 4, entries 1–4) can be readily converted to the corresponding ketones in good yield except

2-chlorophenylethanol. 1-Phenoxy-2-propanone was obtained in good yield (92%) from 1-phenoxy-2-propanol (Table 4, entry 5) after 30 h. 1-Indanol gave 1-indanone in 80% yield after 48 h. The oxidation of primary benzylic alcohols (Table 4, entries 6–8) afforded the corresponding aldehydes in moderate yields. Beyond 36 h, the formed aldehydes were converted into corresponding acids in the case of primary benzylic alcohols. Remarkably, the conversion of cyclic alcohols (Table 4, entries 9–11) to cyclic ketones proceeded efficiently in the present catalytic system. Co(III)-catalyzed oxidation of 1-cyclohexylethanol (Table 4, entry 12) and 1-cyclopropylethanol (Table 4, entry 13) lead to the formation of corresponding ketones in yields of 51% and 83%, respectively. Though the present catalytic system requires a slightly longer reaction time, the efficiency in terms of the yield of products is comparable or higher than the existing Co(III)/TBHP and Ru(II)/TBHP catalytic systems [7,22,23].

It is proposed hypothetically that the catalytic oxidation proceeds through *tert*-butylperoxocobalt(III) species which is formed from solvated intermediate, as shown Scheme 3. The FT-IR spectra of the residue obtained after stirring complex **4** and TBHP at 80 °C for about 24 h showed a strong band at 3371 cm^{-1} and a medium intensity band at 850 cm^{-1} which might be attributed to O–H and
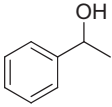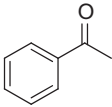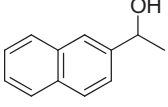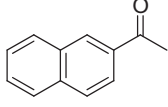
Fig. 4. Effect of solvents upon oxidation of 1-phenylethanol by **4**.
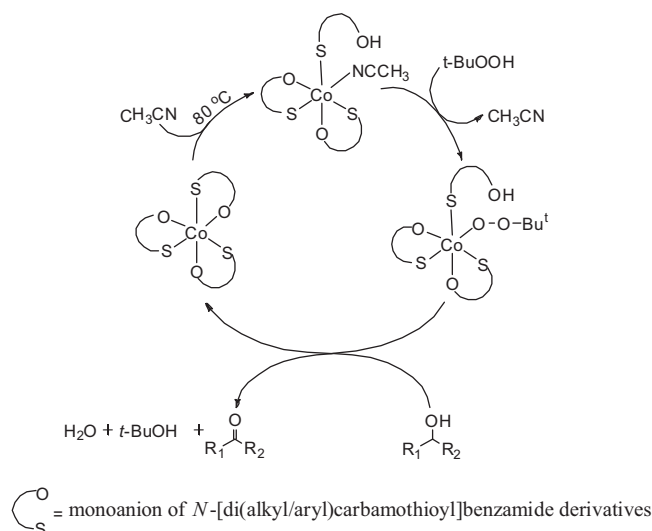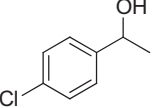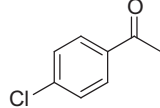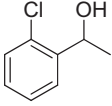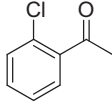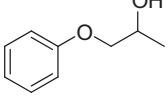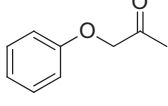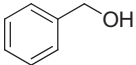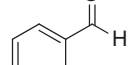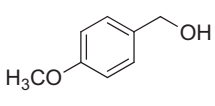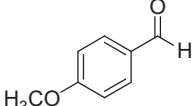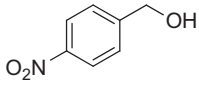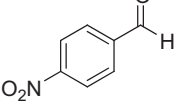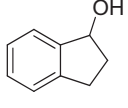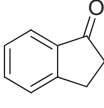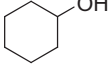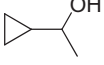
Scheme 3. Possible mechanistic pathway for cobalt(III)-catalyzed oxidation of alcohols.

Table 4
Oxidation of alcohols[a] by **4**.
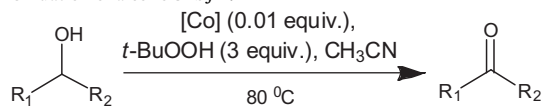
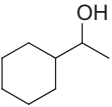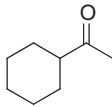| Entry	Substrate	Product	Time (h)	Yield[b] (%)
1			48	93 (91)[c]
2			42	84 (81)[c]
3			36	83
4			42	25
5			30	92
6			24	51
7			36	74
8			36	64
9			48	80
10			36	96
11			30	90
12			48	51
13			30	83

[a] Reaction conditions: alcohol (1 mmol), t-BuOOH (3 mmol), complex 4 (0.01 mmol), acetonitrile (20 mL), 80 °C.
[b] Yield (average of two trials) is determined by GC with area normalization.
[c] Isolated yield is given in parenthesis.

O–O groups respectively present in Co(III)-peroxo intermediate [55,56].

4. Conclusions

In this study, new six coordinated facial *tris*-chelate cobalt(III) complexes containing *N*-[di(alkyl/aryl)carbamothioyl]benzamide derivatives have been prepared and characterized. These complexes were used as catalysts in combination with TBHP for the oxidation of various alcohols at 80 °C. It was expected that catalytic oxidation process passed through Co(III)-*tert*-butylperoxo species. The catalytic reaction results have shown that these complexes are effective catalysts for oxidation of various primary and secondary alcohols in presence of TBHP at 80 °C.

Supplementary data

Supplementary data associated with this article (electronic spectra, representative ^{1}H & ^{13}C NMR spectra of the Co(III) complexes, GC chromatogram, and GC conditions for catalytic studies) can be found in the online version. Crystallographic data (excluding structure factors) for the structure described in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 838004. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.11.019.

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[53] C(4)–H(4)...Cg(C29–C34)^i = 2.91 Å,   C(4)...Cg(C29–C34)^i = 3.736(3) Å, with angle at H(4) = 146°; C(18)–H(18)...Cg(C1–C6)^{ii} = 2.85 Å, C(18)...Cg(C1–C6)^{ii} = 3.685(4) Å, with angle at H(18) = 148°; C(28)–H(28b)...Cg(C29–C34)^{iii} = 2.86 Å, C(28)...Cg(C29–C34)^{iii} = 3.643(3) Å, with angle at H(28b) = 138°; C(38)–H(38c)...Cg(C15–C20)^{iv} = 2.97 Å, C(38)...Cg(C15–C20)^{iv} = 3.702(4) Å, with angle at H(38c) = 132°. Symmetry operations: i = −x, 1 − y, −z; ii = 1 − x, 2 − y,−z; iii = 1 − x, 2 − y, 1 − z; iv = x, −1 + y, z.
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