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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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This paper is dedicated to Prof. Christian Bruneau on the occasion of his 60th birthday.

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ABSTRACT

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 $CoCl_2·6H_2O$ and *N*-[di(alkyl/aryl)carbamothioyl]benzamide in ethanol and characterized by elemental analysis and spectral data (UV/Vis, IR, ^1H & ^{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.

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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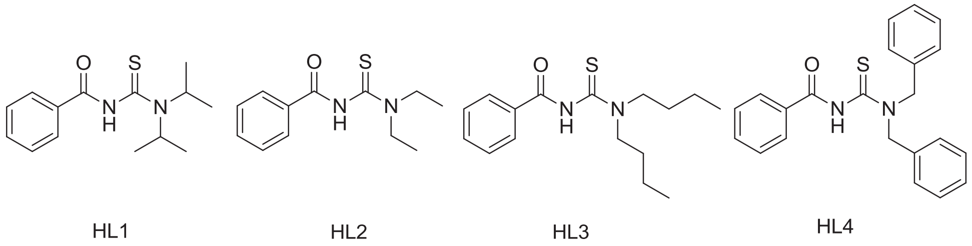

Fig. 1. Structures of ligands employed in this study.

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 $CoCl_2{\cdot}6H_2O$ 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. ^1H 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 ^1H 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. $CoCl_2{\cdot}6H_2O$ (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_3N 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 $CoCl_2{\cdot}6H_2O$ (100 mg, 0.42 mmol) and HL1 (330.5 mg, 1.26 mmol). Yield: 88%, decomposition point: 180 °C, ^1H NMR (acetone-d_6): $\delta = 7.36–8.23$ (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): $\delta = 175.66$, 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 $C_{42}H_{57}CoN_6O_3S_3$ (%): 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 $CoCl_2{\cdot}6H_2O$ (100 mg, 0.42 mmol) and HL2 (296.4 mg, 1.26 mmol). Yield: 85%, decomposition point: 175 °C, ^1H NMR (acetone-d_6): $\delta = 7.28–8.15$ (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): $\delta = 174.64$, 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 $C_{36}H_{45}CoN_6O_3S_3$ (%): 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 $CoCl_2{\cdot}6H_2O$ (100 mg, 0.42 mmol) and HL3 (368.4 mg, 1.26 mmol). Yield: 80%, decomposition point: 225 °C, ^1H NMR (acetone-d_6): $\delta = 7.34–8.21$ (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): $\delta = 175.31$, 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 $C_{48}H_{69}CoN_6O_3S_3$ (%): 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 $CoCl_2{\cdot}6H_2O$ (100 mg, 0.42 mmol) and HL4 (454.2 mg, 1.26 mmol). Yield: 90%, decomposition point: 105 °C, ^1H NMR (acetone-d_6): $\delta = 7.15–8.28$ (m, 45H, aromatic), 5.21 (m, 12H, CH_2) ppm. ^{13}C NMR (acetone-d_6): $\delta = 177.24$, 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 $C_{66}H_{57}CoN_6O_3S_3$ (%): 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_α radiation so that $\theta_{max} = 27.5°$. 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