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Cobalt(II) 4-nitrobenzoates having pyridine as ancillary ligands and their catalytic role in the TBHP oxidation of alcohols

Stutee Chakravorty, Birinchi K. Das *

Department of Chemistry, Gauhati University, Guwahati 781 014, Assam, India

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ABSTRACT

By making use of the Co^{2+}/pyridine (py)/O_2N-4-$C_6H_4CO_2^-$ (4-nbz) system it has been possible to isolate two new complexes with markedly different stabilities: a purple form $[Co(4\text{-nbz})_2(py)_2]$ (**1**) and a pink form $[Co(4\text{-nbz})_2(py)_2(H_2O)_2]$ (**2**). These compounds have been characterized by single crystal X-ray diffraction. Compound **1** may be described as approximately tetrahedral, while compound **2** has Co(II) in a nearly octahedral environment. Both π–π stacking and weak C–H···O interactions appear to contribute to the moderate stability of the tetrahedral complex in the solid state. **2** displays an interesting supramolecular layered structure which is stabilized further by interlayer C–H···O interactions. Facile interconversion between **1** and **2** is found to occur in solid as well as solution phases. Apart from the synthesis, structure and spectral properties of these compounds, catalytic activity of **1** in the *tert*-butyl hydroperoxide (TBHP) oxidation of alcohols is also discussed in this paper.

1. Introduction

Catalytic as well as biological roles of mixed-ligand transition metal complexes containing carboxylate anions and nitrogen base ligands are widespread [1,2]. For example, metal salts of aromatic carboxylic acids are known to display anti-bacterial and anti-fungal properties [3,4]. Previous studies from this laboratory have shown that complexes of cobalt and copper containing carboxylates and pyridines as ligands may act as oxidation catalysts in the transformation of alkylaromatics, alcohols and alkenes under environmentally friendly conditions [5–8]. In this context, we note here that while preparing the cobalt(III) cubane compounds of type $[Co_4O_4(O_2CR)_4L_4]$ for the above purpose a methanolic solution containing Co^{2+}, RCO_2^- and L (which is either pyridine or a substituted pyridine) is generated before producing the cobalt(III) tetramers by subsequent H_2O_2 oxidation [5,6]. However, with R = C_6H_4-4-NO_2 and L = py (C_5H_5N) the above mixture gives a solid product prior to H_2O_2 oxidation. In our efforts to identify this species, which is now known to be a six-coordinate Co(II) complex, we have also been able to isolate a four-coordinate mixed-ligand complex of Co(II) containing two each of nitrobenzoato and pyridine ligands constituting an approximate tetrahedral coordination geometry around the cobalt center.

Formation of both tetrahedral and octahedral complexes is a common feature of the chemistry of cobalt(II). However, in presence of moisture tetrahedral complexes are not easy to obtain as solid products [9]. In fact, tetrahedral complexes among cobalt(II) carboxylates having pyridyl ligands as ancillaries are quite uncommon. A search in the Cambridge Structural Database (CSD) [10] showed only one example of such tetrahedral cobalt(II) complexes, *viz.* bis(η^1-benzoato)bis(4-methylpyridine)cobalt(II) [11], for which a crystal structure is known. Earlier attempts to isolate four-coordinate cobalt(II) species led to the formation of only six-coordinate complexes [12]. In view of favorable thermodynamic effects Co(II) complexes of the octahedral and tetrahedral geometries display facile structural interchange. Solid-state effects including supramolecular interactions are thus likely to be important in the stabilization of the four-coordinate species. Herein we report the syntheses, crystal structures and physicochemical properties of two Co(II) complexes, viz. $Co(4\text{-nbz})_2(py)_2$ (**1**), $[Co(4\text{-nbz})_2(py)_2(H_2O)_2]$ (**2**) containing 4-nbz as monodentate ligands. In addition, we also describe our results on the use of complex **1** in the catalytic oxidation of both primary and secondary alcohols using *tert*-butyl hydroperoxide (TBHP) as the oxidant.

2. Experimental

Materials used in this work were obtained from commercial sources and used as received. $Co(NO_3)_2\cdot 6H_2O$ was obtained from E. Merck (India). The sodium salt of 4-nitrobenzoic acid ($NaO_2CC_6H_4$-4-NO_2) was prepared by neutralizing the acid with NaOH. While benzyl alcohol and 1-phenyl ethanol were obtained from E. Merck (India), 4-nitrobenzyl alcohol, 1-phenyl-1-propanol and TBHP (70% aqueous solution) were purchased from Aldrich (USA). Benzhydrol and benzoin were purchased from Loba Chemie India).

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* Corresponding author. Tel.: +91 361 2570535; fax: +91 361 2700311.
E-mail addresses: Birinchi.Das@hotmail.com, das_bk@rediffmail.com (B.K. Das).

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1-(4′-methyl)-phenyl ethanol was prepared by reduction of the corresponding ketone, 4-methyl acetophenone (E. Merck, India) by literature method [13].

The mid-IR infrared spectra in the 4000–450 cm^{-1} region were recorded using a Perkin–Elmer RX1 FT-IR spectrophotometer as KBr pellets. C–H–N analyses were done using a Perkin–Elmer 2400 Series II CHNS/O instrument. Cobalt analysis was performed gravimetrically by precipitating out cobalt as $Hg[Co(NCS)_4]$ following standard procedure. While the solution UV–Vis spectra were recorded on a Perkin–Elmer Lambda 40 spectrophotometer, the diffuse-reflectance UV–Vis–NIR (200–2600 nm) spectra were obtained using a Hitachi U-4100 spectrophotometer equipped with an integrating sphere. Magnetic susceptibilities were recorded at room temperature using a benchtop Sherwood MK-1 balance by Evans Method. The susceptibility data were corrected for diamagnetism by making use of Pascal's constants. Gas chromatography was done by using a Varian 450-GC instrument equipped with a FID detector and a CP-Sil 8CB capillary column. Retention times of reaction products were confirmed by comparison with authentic samples. Details of single crystal X-ray data collection and structure determination of complexes are described below in a separate section.

2.1. Preparation of $Co(O_2CC_6H_4\text{-}4\text{-}NO_2)_2(C_5H_5N)_2$ (**1**)

$Co(NO_3)_2{\cdot}6H_2O$ (0.5 mmol, 0.145 g) was dissolved in 5 mL of methanol. $NaO_2CC_6H_4\text{-}4\text{-}NO_2$ (1 mmol, 0.189 g) and pyridine (1.5 mmol, ~0.15 mL) were added to this solution and the mixture was stirred at room temperature for 1 h. The purple precipitate was filtered and washed with diethyl ether under suction to obtain a dry crystalline powder. Yield: 61% (based on cobalt). To obtain suitable crystals for single crystal X-ray diffraction work, a 1 mM methanolic solution of $NaO_2CC_6H_4\text{-}4\text{-}NO_2$ (3 mL) was slowly added to 2 mL of a methanolic solution of $Co(NO_3)_2{\cdot}6H_2O$ (0.5 mmol) containing pyridine (1.5 mmol) and the mixture was left undisturbed in a test tube. After 1–2 days a good crop of transparent purple crystals was obtained. The product was stored in a desiccator over fused $CaCl_2$ for further analysis. *Anal.* Calc. for $C_{24}H_{18}N_4O_8Co$ 1: C, 52.43; H, 3.28; N, 10.19. Found: C, 52.01; H, 3.62; N, 10.64%. $\mu_{eff}(298\ K) = 4.15$ BM. IR spectral data (KBr pellet, v_{max}/cm^{-1}): 3427(m), 2924(w), 2852(w), 1624(s), 1588(vs), 1514(vs), 1485(w), 1447(s), 1410(w), 1371(s), 1341(vs), 1317(w), 1215 (w), 1103(w), 1066(w), 1046(w), 1012(w), 876(m), 833(s), 798(m), 762(m), 723(s), 697(s), 642(w) and 572(w). [s, strong; m, medium; w, weak; br, broad].

2.2. Preparation of $[Co(O_2CC_6H_4\text{-}4\text{-}NO_2)_2(C_5H_5N)_2(H_2O)_2]$ (**2**)

2.2.1. Method 1

$Co(NO_3)_2{\cdot}6H_2O$ (3 mmol, 0.873 g), $NaO_2CC_6H_4\text{-}4\text{-}NO_2$ (6 mmol, 1.134 g) and pyridine (6 mmol, ~0.5 mL) were dissolved in water (20 mL) and the mixture was stirred at room temperature for 1 h. The resulting faint orange product was filtered, washed with water and methanol, and dried. Yield: 78% (based on cobalt).

2.2.2. Method 2

The transparent crystals of **1** obtained as above were stored along with the methanolic mother liquor at room temperature for about a month to convert the purple crystals quantitatively to faint orange crystals which are suitable for single crystal X-ray diffraction work. Yield: 61% (based on cobalt). *Anal.* Calc. for $C_{24}H_{22}N_4O_{10}Co$ 2: C, 49.19; H, 3.76; N, 9.57; Co, 10.07. Found: C, 49.10; H, 3.88; N, 9.80; Co, 10.02% (gravimetric). $\mu_{eff}(298\ K) = 5.04$ BM. IR spectral data (KBr pellet, v_{max}/cm^{-1}): 3519(m), 3306(w), 3071(vs), 2924(w), 2852(w), 1614(s), 1599(vs), 1577(vs), 1558(vs), 1624(s), 1588(vs), 1514(vs), 1487(w), 1449(s), 1403(w), 1347(w), 1347(w), 1319(w), 1217(w), 1103(s), 1076(w), 1039(w), 1013(m), 881(m), 797(s), 760(m), 724(s), 701(s), 630(w) and 526(w). [s, strong; m, medium; w, weak; br, broad].

2.3. X-ray crystallographic procedures

Crystals of suitable size were picked for intensity data collection at room temperature using graphite-monochromatized Mo–Kα radiation ($\lambda = 0.71073$ Å) at 293 K on a Bruker SMART CCD diffractometer [14]. The crystals were stable during the measurements at room temperature, no intensity decay was observed. The structures were solved by direct methods (SHELXS-97) and standard Fourier techniques and refined on F^2 using full matrix least squares techniques (SHELXL-97) [15] using the WINGX [16] platform available for personal computers. All non-hydrogen atoms were refined with anisotropic displacement parameters. The aromatic hydrogen atoms were placed at calculated positions and refined by making use of a riding model. The hydrogen atoms of the water molecules for compound **2** were located in difference Fourier maps and refined with isotropic atomic displacement parameters. The crystal data and structure refinement details are given in Table 1. The crystal structures were analyzed using MERCURY [17] and PLUTON [18], while the structural diagrams were drawn using Diamond 3 [19].

2.4. Oxidation of alcohols: typical procedure

To a stirred solution of benzyl alcohol (0.54 g, 5 mmol) in CH_3CN solvent (5 mL) taken in a two-necked round-bottomed flask equipped with a reflux condenser was suspended 1.5 mol% (0.0412 g) of complex **1** (0.075 mmol). 2 mL (~15 mmol) of 70% aqueous *tert*-butyl hydroperoxide (TBHP) was then added to the above mixture, and the contents were stirred at 82 °C for 5 h. The course of the reaction was monitored by TLC in all cases using petroleum ether–ethyl acetate (9:1 v/v) as the solvent system. At the completion of the reaction, the excess TBHP was destroyed by adding sodium metabisulfite into the reaction mixture and then the mixture of products was extracted with diethyl ether. After

Table 1
Crystallographic data for $Co(4\text{-}nbz)_2(py)_2$ (**1**) and $Co(4\text{-}nbz)_2(py)_2(H_2O)_2$ (**2**).

	1	**2**
Formula	$C_{24}H_{18}N_4O_8Co$	$C_{24}H_{22}CoN_4O_{10}$
Formula weight	549.35	585.39
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$
a (Å)	14.9862 (6)	14.4946 (16)
b (Å)	6.3167 (2)	11.6071 (13)
c (Å)	24.8559 (10)	7.9534 (10)
β (°)	91.964 (4)	105.636 (4)
V ($Å^3$)	2351.56 (15)	1288.6 (3)
Z	4	2
Crystal size (mm)	0.43 × 0.23 × 0.12	0.48 × 0.28 × 0.18
D_{calc} (g cm^{-3})	1.552	1.509
μ (Mo Kα) (mm^{-1})	0.789	0.730
$T_{minimum}/T_{maximum}$	0.7279/9113	0.7208/0.8798
Reflections collected (unique), R_{int}	11652 (2746), 0.0238	15224 (3060), 0.0342
Parameters refined	168	187
R_1/wR_2 (all data)	0.0405/0.0824	0.0994/0.2673
R_1/wR_2 ($F_o \geqslant 4\sigma(F_o)$)	0.0312/0.0773 (2292 reflections)	0.0874/0.2589 (2455 reflections)
Goodness of fit on F^2	1.034	1.078
$(shift/esd)_{max}$	0.001	0.000
$\Delta\rho_{maximum,minimum}$ (e $Å^{-3}$)	0.294, −0.185	0.803, −0.606

R and R_w values are for all unique data; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = [2F_c^2 + Max(F_o^2,0)]/3$.

removal of most of the diethyl ether solvent, the acid part of the product was separated from the above solution via extraction with a saturated $NaHCO_3$ solution and then by adding conc. hydrochloric acid to the resultant aqueous solution the acid was obtained as a pure solid. For other alcohols, after completion of the reaction, similar work-up procedures were followed up to the diethyl ether extraction of product(s). The extract was then dried with anhydrous Na_2SO_4 and after removal of the solvent, the crude product was purified by flash chromatography using petroleum ether-ethyl acetate (9:1 v/v) as the eluent.

3. Results and discussion

3.1. Preparation of complexes

Syntheses of the Co(II) complexes **1** and **2** have been accomplished via simple mixing of a Co(II) salt with the sodium salt of 4-nitrobenzoic acid and pyridine at room temperature. The synthetic procedures followed by us are illustrated in Scheme 1. For the self-assembly of the purple colored species **1**, $Co(NO_3)_2·6H_2O$, $NaO_2CC_6H_4$-4-NO_2 and pyridine were reacted in a 1:2:3 molar ratio in methanol. It is important (i) to keep the Co^{2+}:py ratio at 1:3, (ii) to use only a small volume of methanol and (iii) to isolate the product from the reaction mixture at the earliest. While storing the reaction mixture along with the purple crystals of **1** for over three weeks, complete conversion of the purple crystals to faint orange crystals of **2** occurs. The crystalline species produced by this route is same with samples of **2** prepared via an alternative route by making use of the above reaction mixture in the 1:2:2 ratio in an aqueous medium.

In open air the purple crystals of **1** slowly transform into opaque blocks of pink colour. But, samples of **1** are indefinitely stable if stored in tightly closed vials or in a dry atmosphere. Compound **2** is stable in air in the solid state; however, it dissolves readily in dichloromethane and acetonitrile to form purple solutions containing **1**. From these solutions, it is possible to precipitate out **1** by adding petroleum ether or diethyl ether. It is believed that favorable thermodynamic effects allow Co(II) complexes to undergo facile structural interchange between the octahedral and tetrahedral coordination geometries. On one hand, solid-state effects including supramolecular interactions are likely to be important in the stabilization of the four-coordinate species relative to the six-coordinate complex, while substitutional lability of Co(II) leads to the conversion of the purple tetrahedral species to the pink octahedral species under moist conditions.

3.2. Crystal structures

X-ray crystallographic studies have shown that compound **1** is a nearly tetrahedral 4-coordinate cobalt(II) complex (Fig. 1 and Table 2) wherein the coordination sphere consists of two pyridyl N atoms and two oxygen atoms from two monodentate carboxyl groups. The cobalt atom lies on a twofold axis of symmetry and thus the asymmetric unit in the crystal structure has one each of the 4-nbz and py ligands. While the Co–O distance is 1.970(1) Å, the Co–N distance stands at 2.048(1) Å. The Co–O bond for the monodentate nitrobenzoato ligands in 1 is shorter than the corresponding distances of 2.183(1) Å and 2.091(2) Å observed for the same ligand in octahedral Co(II) complexes [20,21]. However, the observed Co–O bond is somewhat longer than the corresponding distance of 1.922 Å found in the structurally related complex bis(η^1-benzoato)bis(4-methylpyridine)cobalt(II) [11]. The observed Co–N bond distance in **1** also compares well with the Co–N

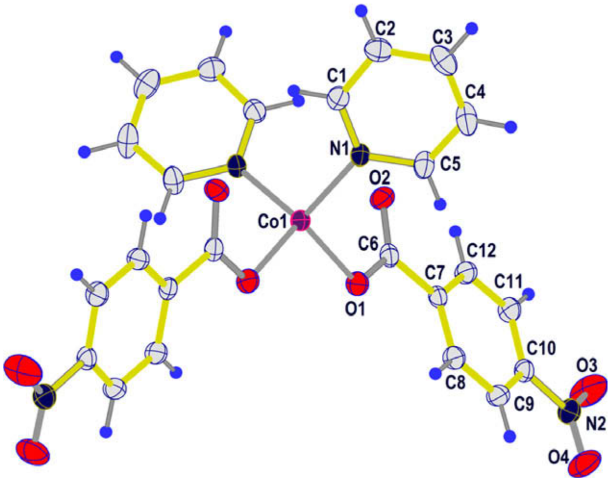
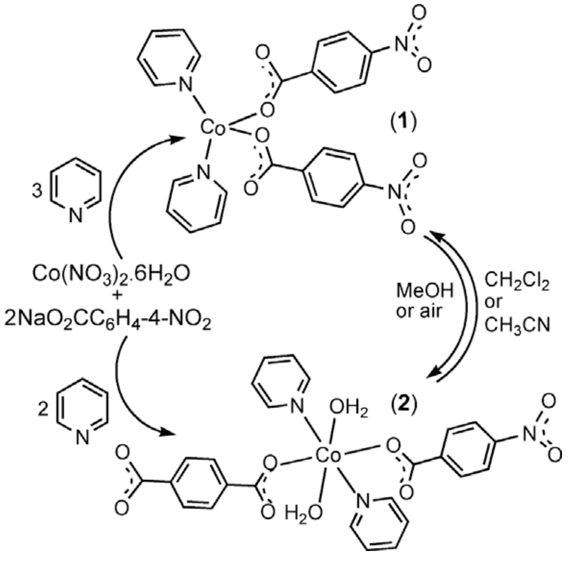


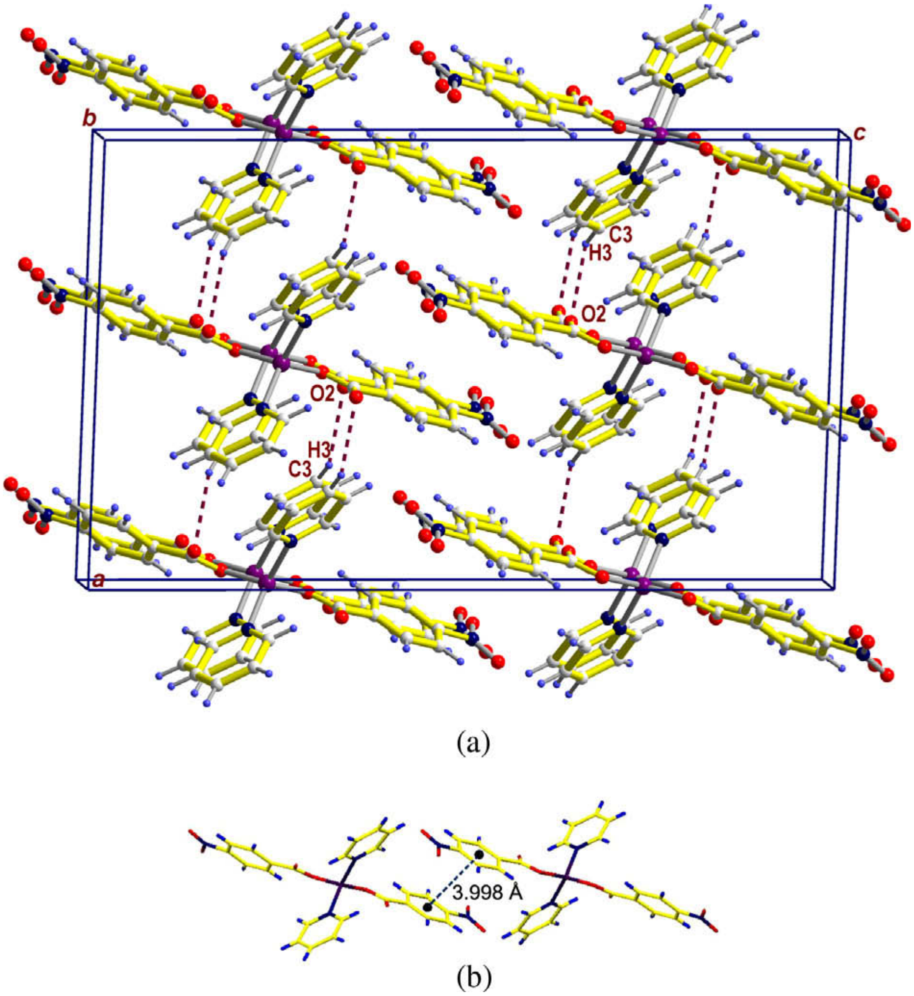
Fig. 1. Molecular structure of $Co(O_2CC_6H_4\text{-}4\text{-}NO_2)_2(C_5H_5N)_2$ (**1**) with non-hydrogen atoms drawn as ellipsoids at 25% probability level.

Table 2
Selected interatomic distances (Å) and angles (°) for $Co(O_2CC_6H_4\text{-}4\text{-}NO_2)_2(C_5H_5N)_2$ (**1**), $Co(O_2CC_6H_4\text{-}4\text{-}NO_2)_2(C_5H_5N)_2(H_2O)_2$ (**2**).

Compound ***1***			
Co(1)–O(1)	1.9704(12)	Co(1)–N(1)#1	2.0482(14)
O(1)–C(6)	1.281(2)	O(2)–C(6)	1.229(2)
O(3)–N(2)	1.210(2)	O(4)–N(2)	1.211(2)
O(1)–Co(1)–O(1)#1	98.71(7)	O(1)-Co(1)-N(1)	106.12(5)
O(1)–Co(1–N(1)#1	120.88(6)	N(1)#1–Co(1)–N(1)	105.25(8)
C(6)–O(1)–Co(1)	109.36(10)	C(1)–N(1)–Co(1)	121.48(11)
C(5)–N(1)–Co(1)	120.37(12)	O(1)–C(6)–O(2)	123.69(15)
O(3)–N(2)–O(4)			
#1 −*x* + 1,y, −*z* + 3/2			
Compound ***2***			
Co(1)–O(1)	2.082(3)	Co(1)–O(5)	2.107(4)
Co(1)–N(1)	2.164(4)	O(2)–C(6)	1.259(6)
O(1)–C(6)	1.247(6)	O(4)–N(2)	1.204(14)
O(3)–N(2)	1.154(13)		
O(1)–Co(1)–O(5)	89.09(15)	O(1)#1–Co(1)–O(5)	90.91(15)
O(1)–Co(1)–N(1)#1	91.54(16)	O(5)–Co(1)–N(1)#1	92.93(16)
O(5)#1–Co(1)–N(1)#1	87.07(16)	O(1)–Co(1)–N(1)	88.46(16)
O(1)–C(6)–O(2)	126.3(5)	O(3)–N(2)–O(4)	122.0(9)
#1 −*x*, −*y*, −*z*			



Scheme 1.



(a)

(b)

Fig. 2. (a) Crystal packing diagram showing the C–H·· O and π–π interactions in the structure of compound **1**. (b) centroid–centroid proximity of 4-nbz ring planes.

distances reported for various tetrahedral Co(II) complexes with pyridine ligands: e.g., [Co(η^1-$O_2CC_6H_5$)$_2$(4-Mepy)$_4$], 2.034 Å [11]; [Co(py)$_4$]$^+$, 2.00(2) Å [22] and [Co(py)Cl_3]$^-$, 2.059(9) Å [23]. The shorter O(2)–C(6) bond compared with O(1)–C(6) in **1** (Table 2) agrees well with its expected partial double bond character in the monodentate mode of coordination of the carboxyl group, which also is responsible for the appearance of $\nu(COO)_{asym}$ at a relatively higher energy of 1624 cm^{-1}.

The O–Co–O, N–Co–N and O–Co–N bond angles of 98.71(7)°, 105.25(8)° and 106.12(5)°/120.88(6)°, respectively in **1** deviate considerably from the ideal tetrahedral angle. The only other structurally characterized tetrahedral Co(II) complex having the [Co(carboxylate)$_2$(pyridine)$_2$] type composition, [Co(η^1-$O_2CC_6H_5$)$_2$-(4-Mepy)$_4$], [11] also shows substantial distortion from ideal tetrahedral geometry. For this complex, the O–Co–O, N–Co–N and O–Co–N bond angles are reported to be 135.00°, 103.05° and 95.15°/112.73°. It appears that the elongation of the Co–O and Co–N bonds in **1** compared to the corresponding distances in [Co(η^1-$O_2CC_6H_5$)$_2$(4-Mepy)$_4$] may be due the inductive effects of the substituents at the 4-positions of the carboxylato and pyridyl ligands in these two complexes. On the other hand, the differences in the bond angles in the coordination spheres of the cobalt centers are believed to be related to crystal packing effects.

A closer look reveals that intermolecular interactions play an important role in the crystal structure of complex **1**. As shown in Fig. 2, the interplanar (centroid to centroid) distance of 3.998 Å in case of the phenyl rings in the $O_2CC_6H_4$-4-NO_2 moieties is suggestive of π–π interactions [24]. On the other hand, the long centroid to centroid separation of 4.805 Å for the pyridine rings are quite long for such an interaction. But, C–H···O interactions between the C–H group at the para position of the pyridine ring

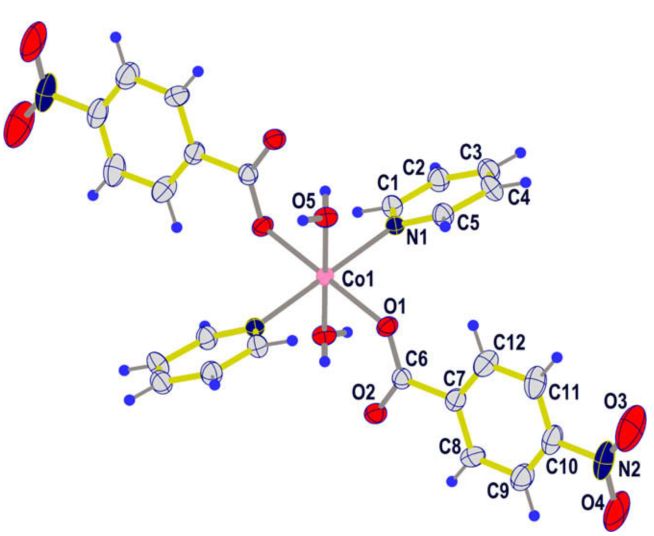


Fig. 3. Molecular structure of $Co(O_2CC_6H_4\text{-}4\text{-}NO_2)_2(C_5H_5N)_2(H_2O)_2$ (**2**) with non-hydrogen atoms drawn as ellipsoids at 25% probability level.

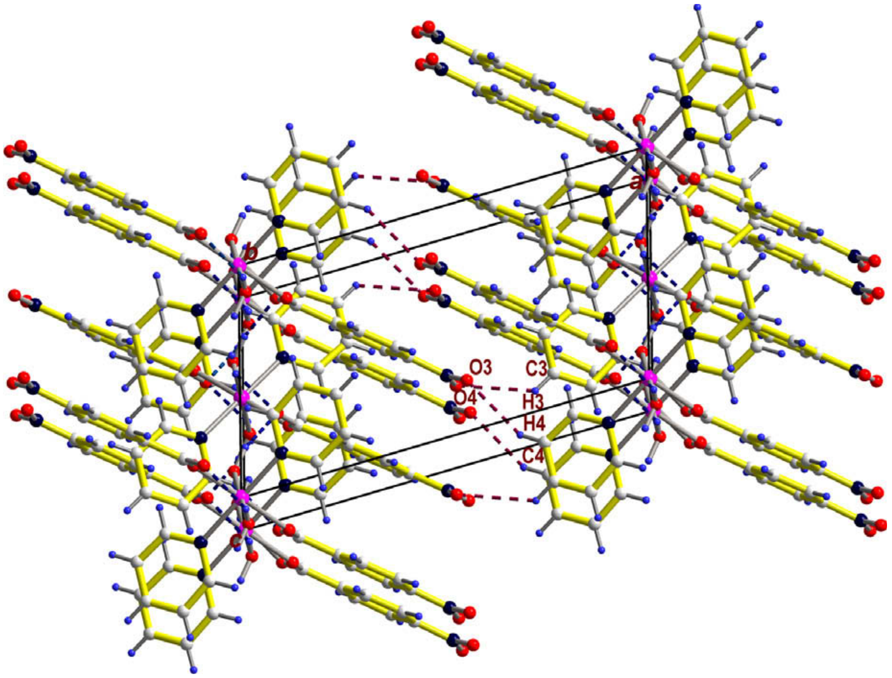


Fig. 4. Unit cell packing diagram of **2** showing C–H·· O interactions between 2-D sheets. The **C**·· **O** separations and C–H·· O angles for the two distinct interactions in the crystal are 3.363/3.502 Å and 127.84/151.06°, respectively.

and the uncoordinated oxygen atom of the carboxylato ligands from an adjacent molecule appear to provide a significant supramolecular force in determining the crystal structure of the tetrahedral complex. The weak C–H···O hydrogen bridges (2.652 Å) are believed to be responsible for the deviation of the nitrobenzoato ligands from overall molecular planarity. It is seen that the planar nitro and carboxyl groups of the nitrobenzoato ligand are twisted away from the phenyl ring plane by 4.5(3)° and 11.1(2)°, respectively. Such deviations from overall planarity of a coordinated ligand have been correlated earlier with higher lattice enthalpy effects and enhanced solid-state stability in metal terephthalate complexes [25].

Both identity and composition of compound **2** have been ascertained by X-ray crystallography. The asymmetric unit of the crystal structure consists of a half of the formula unit, with the Co atom lying at the crystallographic center of symmetry (0 0 0) and all others at general positions (*x*, *y*, *z*). The six-coordinate Co(II) complex of $Ma_2b_2c_2$ type has all three ligand pairs in mutually trans positions. (Fig. 3). The carboxylate anions coordinate in a monodentate fashion as in related Co(II) complexes containing $CoO_2N_2O_2$ coordination spheres [21,22,26–28]. Unlike in the case of **1**, the carboxyl and nitro groups are nearly coplanar with the phenyl ring plane in the nitrobenzoato ligand present in **2**. As expected, the observed Co–O(carboxylate) and Co–N(pyridine) bond lengths in compound **2** are longer than the corresponding distances for 4-coordinate Co(II) in **1** (Table 2). The Co(II)–O and Co(II)–N distances observed in **2** are comparable with values in other related complexes [21,22]. The deviations of the cis(O–Co–N) and cis(O–Co–O) bond angles in the coordination sphere from the ideal value of 90° are small. However, on the basis of disparate M–L distances, which may also be subject to Jahn–Teller effect for the d^7 ion, it is useful to point out that the coordination geometry around the cobalt(II) center is far from idealized octahedral.

Fig. 4 shows that the crystal structure of **2** is two-dimensional (2-D) in which hydrogen-bonded layers run along the crystallographic *bc* plane. Both intra- and intermolecular O–H···O bonds (Table 3) between the coordinated water molecules and the uncoordinated carboxyl oxygen atoms are responsible for the formation of the supramolecular layers as illustrated in Fig. 5. The intricate patterns of hydrogen bonds in the solid-state structure of **2** can be understood and analyzed by graph-set theory [29]. It is possible to identify an intramolecular hydrogen-bonded ring denoted by S(6) which is formed by the 'Co–O(carboxylate)–C–O(carboxylate)–(OH_2)' moiety. The coordinated water molecule is further linked with the uncoordinated oxygen atom of the carboxylate ligand of an adjacent molecule via intermolecular hydrogen bonding to form a supramolecular chain. This chain is describable as $C_2^1(4)$. The superscripts and subscripts in the symbol are respectively the number of hydrogen bond acceptors and hydrogen bond donors. A 20-membered ring formed by periodic repetition of this chain generates a cyclic $R_8^4(20)$ motif. This ring constitutes a characteristic pattern repeating within 2-D supramolecular sheets of **2**.

In addition to the moderately strong O–H···O hydrogen bonds, weaker C–H···O interactions also characterize the crystal structure under discussion. These intermolecular hydrogen bridges are found to involve the O atoms of the nitro groups and aromatic C–H groups from adjacent layers (Fig. 4). It appears to us that although the nitro groups of the 4-nitrobenzoate ligands in **1** are not involved in any significant intermolecular interaction, the C–H···O interactions involving the nitro groups are playing a crucial structure directing role in **2**. This suggests that the NO_2 groups in the latter compound are more basic due to the somewhat weaker cobalt–oxygen bonds for the carboxylato ligands.

Table 3
O–H·· O hydrogen bonds for present in the crystal structure of **2**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(5)–H(5A) ·· O(2)#1	0.67(8)	2.14(8)	2.698(6)	142(8)
O(5)–H(5B) ·· O(2)#2	0.94(6)	1.84(6)	2.742(6)	159(5)

Symmetry transformations used to generate equivalent atoms: #1 −*x* + 1, −*y* + 1, −*z*. #2 −x + 1, *y* + 1/2, −z + 1/2.

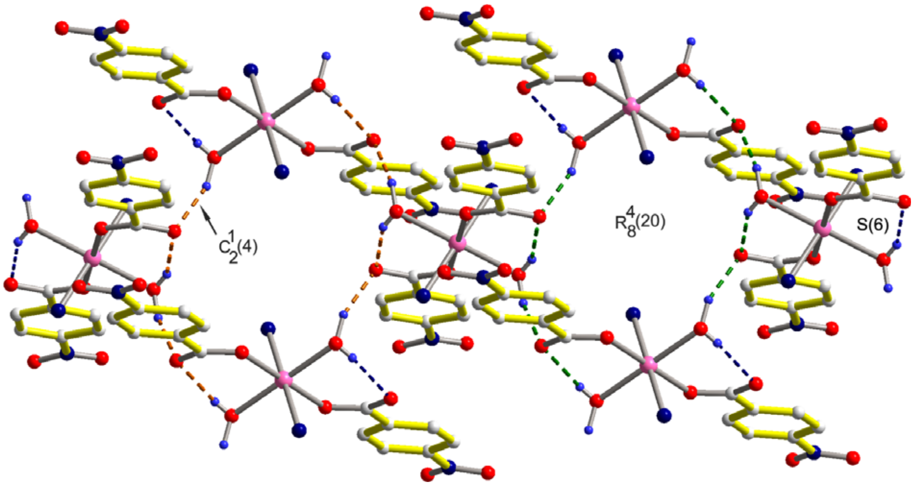


Fig. 5. Hydrogen bond patterns with graph-set descriptors in the crystal structure of **2**. For clarity, pyridine ligands have been denoted by only the coordinated N atoms.

3.3. Electronic spectral properties

The visible band in tetrahedral Co(II) complexes generally appears as a multiple absorption envelope in the 500–700 nm range, whereas the absorption band of octahedral Co(II) complexes in the visible region appears near 500 nm and hence a clear cut distinction between tetrahedral and octahedral geometry of cobalt(II) complexes can be made on the basis of their electronic spectra [30,31]. We have studied the electronic spectra of complexes **1** and **2** in both solid as well as solution phases.

The solid-state UV–Vis–NIR spectra recorded for **1** and **2** are shown in Fig. 6. The spectra in both cases are composed of two broad absorptions occurring in the visible and near infrared regions respectively. The electronic spectra for the complexes have also been measured in the solution phase (Table 4). Comparing the visible band for **1** with the corresponding band observed for its CH_2Cl_2 solution we note the difference in shape between the absorption bands displaying λ_{max} values of 582 nm and 558 nm respectively in the solid and solution phases. This observation suggests a structural reorganization occurring upon dissolution. However, the molar absorptivity indicates that the species retains its tetrahedral coordination sphere in the solution phase as well. The observed λ_{max} value of 517 nm for an MeOH solution of **2** is also quite different from the corresponding band in the solid-state spectrum with λ_{max} = 476 nm to suggest a minor structural change in the complex species present in solution. The broad near IR absorptions in both cases are attributable to the $\nu_2[^4A_2 \rightarrow {}^4T_1(F)]$ and $\nu_1[^4T_{1g}(F) \rightarrow {}^4T_{2g}]$ transitions respectively for **1** and **2**. Moreover, bands at 291 nm and 288 nm (not shown in Fig. 6) are due to the π–π^* transitions of the organic groups present in complexes **1** and **2**, respectively.

Rather interestingly, both complexes show nearly identical spectra in CH_2Cl_2. On the basis of absorption intensities, and band shapes observed it is easy to conclude that the CH_2Cl_2 solutions of both complexes contain the same species. The CH_3CN solution also gives nearly identical UV–Vis spectrum which is characteristic of tetrahedral cobalt(II) complexes. On the other hand, complex **2** in

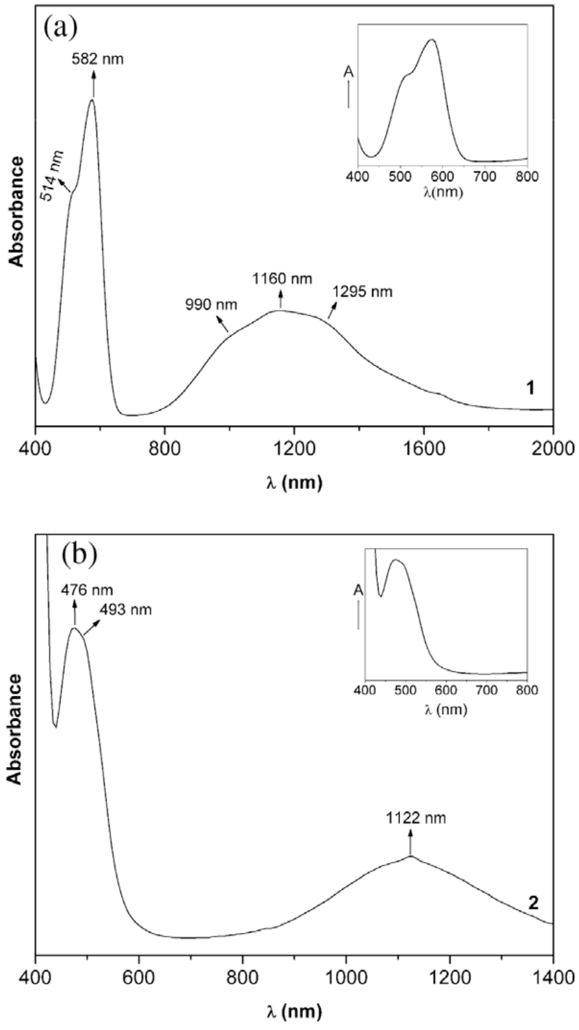
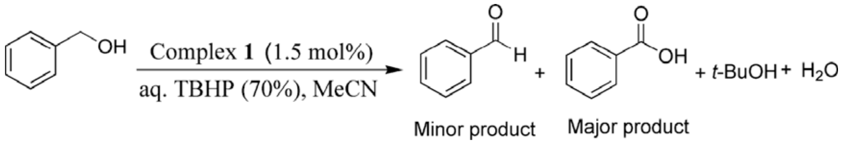


Fig. 6. Solid-state UV–Vis–NIR spectra of **1** (a) and **2** (b).

Table 4
Solution-phase electronic spectral data on **1** and **2** in the 400–800 nm range.

	λ_{max}, nm (ε, L mol^{-1} cm^{-1})	
	1	**2**
CH_2Cl_2	593 (sh) 558 (125) 522 (sh)	593 (sh) 560 (126) 521(sh)
CH_3CN	591(sh) 566(85) 528(sh)	
MeOH		517 (4.8) 474 (sh)



Scheme 2.

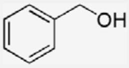
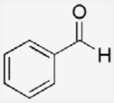
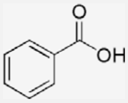
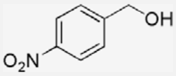
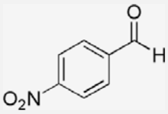
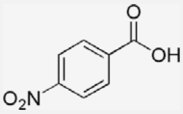
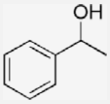
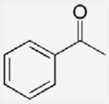
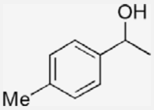
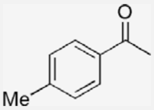
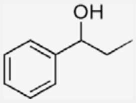
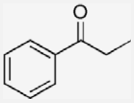
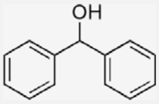
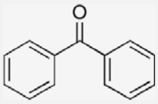
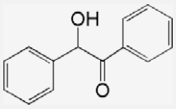
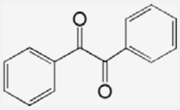
methanol gives λ_{max} = 517 nm with $\varepsilon \approx 4.8$ L mol^{-1} cm^{-1} which is characteristic of cobalt(II) in an octahedral environment [32]. Clearly, the species present in the pink methanolic solution and the purple dichloromethane solution of **2** are different. This leaves no doubt that the absorbing complex species present in a solution of [Co(4-nbz)$_2$(py)$_2$(H$_2$O)$_2$] (**2**) in CH_2Cl_2 is actually [Co(4-nbz)$_2$(py)$_2$] (**1**). The nonpolar solvent medium induces the molecules of **2** to shed the coordinated water molecules since in terms of CFSE the 6- and 4-coordinate complexes are not too different. This information coupled with the observed conversion of crystals of the tetrahedral complex, **1**, in hydrous methanol to the octahedral species **2**, demonstrate clearly that the four- and six-coordinate complexes are interconvertible both in the solid as well as solution states.

Table 5
Optimization of conditions in the TBHP oxidation of benzyl alcohol catalyzed by complex **1**.

Entry	Oxidant amount (mL)	Catalyst amount (mol%)	Temperature (°C)	Time (h)	Product yields (%)[a]	
					Benzaldehyde	Benzoic acid
1	1	1.5	82	5	33	48
2	2	0.5	82	5	7	64
3	2	1	82	5	7	77
4	**2**	**1.5**	**82**	**5**	**5**	**88**
5	2	1.5	27	18	49	4

Reaction conditions: benzyl alcohol = 5 mmol (0. mL); solvent (CH_3CN) =5 mL.
[a] GC yields.

Table 6
TBHP oxidation of alcohols catalyzed by [Co(4-nbz)$_2$(py)$_2$] (**1**).

Substrate	Time (h)	Products	Isolated yields (%)	Melting point (°C)
	5		4	(*l*)
			83	121
	5		15	104
			63	237
	2		75	(*l*)
	2		65	(*l*)
	4		85	(*l*)
	3		85	49
	4		93	95

Reaction conditions: substrate, 5 mmol; CH_3CN, 5 mL; catalyst amount, 1.5 mol%; aq. TBHP (70%), 2 mL; reaction temperature, 82 °C. *l*, liquid product.

3.4. Catalytic studies

In view of the solubility of complex **1** in acetonitrile we found it instructive to examine if the complex is active as a homogeneous catalyst in the oxidation of alcohols. In presence of a catalytic amount (1.5 mol%) of complex **1**, aqueous TBHP (70%) has been found to effectively oxidize both primary and secondary alcohols in acetonitrile medium. No other additives are required for the oxidation of alcohols. Scheme 2 illustrates the reaction involving benzyl alcohol.

In Table 5 we present the results of our detailed studies on benzyl alcohol oxidation mediated by complex **1**. As may be seen from entry 5 in the table, the rate of the reaction at room temperature is slow and even after 18 h of reaction time, conversion of benzaldehyde is only 53%. However, unlike in the reactions carried out at 82 °C, benzaldehyde is the major product forming at 92% selectivity. In order to study the effect of the amount of catalyst with respect to substrate, the benzyl alcohol oxidation was studied at three different catalyst concentrations. On the basis of these studies, the highest conversion of benzyl alcohol is observed with 5 mmol of substrate, 15 mmol (2 mL) of TBHP and 1.5 mol% of the catalyst dissolved in 5 mL of acetonitrile at 82 °C. The substrate conversion also increases from 81% to 93% when the amount of TBHP is increased from 1 to 2 mL. The reaction carried out in the absence of the catalyst leads to only 2% conversion of the substrate.

As shown by the data presented in Table 6, carboxylic acids are found to form as major products as a result of the oxidation of primary alcohols. In case of secondary alcohols, the corresponding carbonyl compounds are obtained exclusively. These results thus indicate that complex **1** is an effective catalyst in the oxidation of both primary as well as secondary alcohols. In earlier studies involving cobalt(II) complexes as catalysts for alcohol oxidation, other authors also reported the formation of both aldehyde as well as carboxylic acid as products from primary alcohols [33,34].

4. Conclusions

Synthesis and crystal structure of two cobalt(II) 4-nitrobenzoates having py as ancillary ligands are described. Spectral evidences suggest that under suitable conditions the four- and six-coordinate complexes undergo facile interconversion between themselves. Complex **1** acts as a catalyst in the TBHP oxidation of primary and secondary alcohols, to form both aldehydes and carboxylic acids from primary alcohols and only ketones from secondary alcohols.

5. Supplementary data

CCDC 760120 and 760121 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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