

A mononuclear cobalt(II) hydroxo complex: synthesis, molecular structure, and reactivity studies

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Received: 29 March 2008 / Accepted: 28 May 2008 / Published online: 18 September 2008
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Abstract A novel Co(II) hydroxo complex $\text{Co}\{\text{HB}(3\text{-}^t\text{Bu-5-}^i\text{Prpz})_3\}(\text{OH})$ **4** {where $\text{HB}(3\text{-}^t\text{Bu-5-}^i\text{Prpz})_3$ = hydrotris(3-*tert*-butyl-5-isopropylpyrazol-1-yl)borate} has been prepared and its molecular structure has been determined by X-ray crystallography. This complex is mononuclear with distorted tetrahedral geometry. The reaction of CO_2 with $\text{Co}\{\text{HB}(3\text{-}^t\text{Bu-5-}^i\text{Prpz})_3\}(\text{OH})$ resulted in the formation of a μ -carbonato bridged binuclear complex $[\text{Co}\{\text{HB}(3\text{-}^t\text{Bu-5-}^i\text{Prpz})_3\}]_2(\text{CO}_3)$ wherein the carbonate group is bound to both metal centers in an asymmetrical manner. In order to explore the role of labile metal complexes in promoting ester hydrolysis, complexes $[\text{Co}\{\text{HB}(3,5\text{-}^i\text{Pr}_2\text{pz})_3\}]_2(\text{OH})_2$ and $\text{Co}\{\text{HB}(3\text{-}^t\text{Bu-5-}^i\text{Prpz})_3\}(\text{OH})$ have been used as catalysts in the hydrolysis of both carboxylate as well as phosphate esters. The product of 4-nitrophenylacetate hydrolysis with $\text{Co}\{\text{HB}(3\text{-}^t\text{Bu-5-}^i\text{Prpz})_3\}(\text{OH})$ was isolated as four coordinate $\text{Co}\{\text{HB}(3\text{-}^t\text{Bu-5-}^i\text{Prpz})_3\}(\text{OC}_6\text{H}_4\text{-4-NO}_2)$ **6**, whereas the reaction of 4-nitrophenyltrifluoroacetate with $[\text{Co}\{\text{HB}(3,5\text{-}^i\text{Pr}_2\text{pz})_3\}]_2(\text{OH})_2$ resulted the formation of the six coordinate $\text{Co}\{\text{HB}(3,5\text{-}^i\text{Pr}_2\text{pz})_3\}(\text{OC}_6\text{H}_4\text{-4-NO}_2)(\text{MeCN})_2$ species.

Introduction

A large number of Zn^{2+} containing hydrolytic enzymes are known which catalyze the hydrolysis or hydration reactions [1–3]. Among these, some well-studied hydrolases are—carbonic anhydrase (CA), carboxypeptidase A (CPA), angiotensin-converting enzymes, alkaline phosphatase, and the lyases [4–7]. The active site of carbonic anhydrase consists of a monomeric zinc ion, coordinated to three histidyl nitrogen atoms and a water molecule. The well-accepted mechanism involves deprotonation of the coordinated water molecule to generate a hydroxide ion on the zinc, which reacts with CO_2 to give bicarbonate. While the zinc-containing carbonic anhydrase is the most effective, the zinc ion in this enzyme has been substituted with other divalent metal ions. Some of these metal-substituted carbonic anhydrases are also effective for the hydration of CO_2 with the order as— $\text{Zn}(\text{II}) > \text{Co}(\text{II}) \gg \text{Ni}(\text{II}) \approx \text{Mn}(\text{II}) > \text{Cu}(\text{II}) \approx 0$. This order of reactivity suggested that the cobalt substituted carbonic anhydrase is less effective than zinc-containing carbonic anhydrase but more effective than other metal substituted carbonic anhydrases. In the above-mentioned hydrolytic enzymes, it is well known that the active species in hydration/hydrolytic reaction is the mononuclear hydroxide. Various examples of the hydrolytic reactions catalyzed by cobalt(III) complexes are available in the literature [8–11] but to the best of our knowledge there is no example with cobalt(II) complexes.

Attempts to mimic the metal coordination environment in carbonic anhydrase and other zinc-containing enzymes were met with limited success [12–14] before the first report of LZnOH , where $\text{L} = \text{KHB}(3\text{-}^t\text{Bu-5-Mepz})_3$ [15]. Also, a series of structurally characterized binuclear hydroxo complexes, capable of fixing the atmospheric carbon dioxide, has been reported by Kitajima et al. [16].

Electronic supplementary material The online version of this article (doi:10.1007/s11243-008-9143-2) contains supplementary material, which is available to authorized users.

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The structurally characterized mononuclear hydroxo complexes with pyrazolylborate are limited in the literature. Hikichi et al. reported the crystal structure of mononuclear iron hydroxide in 1997 [17], whereas Fujisawa and co-workers reported the crystal structure of mononuclear copper hydroxide having pyrazolylborate as supporting ligand [18]. The present paper reports the preparation of a cobalt(II) hydroxide complex and its reaction with carbon dioxide and variety of different esters. The study suggested that the present cobalt(II) hydroxo complex is capable of both CO₂ hydration as well as ester hydrolysis.

Experimental

Materials and methods

All solvents used were purified by literature methods [19]. The cobalt nitrate hexahydrate (reagent grade) was purchased from E. Merck. The other reagents of the highest grade commercially available were used without further purification. All reactions were carried out under nitrogen. The potassium salt of hydrotris(3-*tert*-butyl-5-isopropylpyrazol-1-yl)borate [KHB(3-^tBu-5-ⁱPrpz)₃] [20] **1** and [Co{HB(3,5-ⁱPrpz)₃}₂(OH)₂] **2** were prepared by literature method [16]. IR measurements were carried out in the range of 400–4,000 cm⁻¹ as KBr pellets using Perkin-Elmer 2000 FT-IR spectrometer. The electronic spectra were recorded on a Lambda 35 Perkin Elmer UV–visible spectrometer. Mass spectra were recorded on a Finnigan MAT 8200 instrument (for the EI spectra, 70 eV). Temperature-dependent magnetic susceptibilities of powdered samples were measured by using a SQUID magnetometer (Quantum Design) at 1.0 T (2–290 K). Corrections for underlying diamagnetism were made by using tabulated Pascal constants. The X-ray data collections for **4**, **5**, and **6** were performed on Siemens Smart-CCD diffractometer, while for **7** on Bruker Smart-CCD diffractometer.

Preparation of [Co{HB(3-^tBu-5-ⁱPrpz)₃}](NO₃) (**3**)

A solution of Co(NO₃)₂ · 6H₂O (0.58 g, 2.00 mmol) in methanol (25 mL) was added to a stirred solution of [KHB(3-^tBu-5-ⁱPrpz)₃] (1.09 g, 2.00 mmol) in dichloromethane (15 mL). The mixture was stirred for 4 h. Then, the precipitate was filtered off and dried under vacuum for several hours. Yield 0.46 g (37%). Anal. Calcd. for C₃₀H₅₂N₇O₃BCo: C, 57.3; H, 8.3; N, 15.6. Found: C, 58.6; H, 8.8; N, 15.5. IR (KBr, cm⁻¹): ν(BH) 2593, ν_{as}(NO₃) 1528, ν_s(NO₃) 1275. UV–vis (toluene, nm, ε/M⁻¹ cm⁻¹): 292 (1188), 602 (330). EI-MS (*m/z*): 628[Co(NO₃){HB(3-^tBu-5-ⁱPrpz)₃}], 565[Co{HB(3-^tBu-5-ⁱPrpz)₃}]⁺. Magnetic moment (290 K): 3.70 B.M.

Preparation of [Co{HB(3-^tBu-5-ⁱPrpz)₃}](OH) (**4**)

A solution of **3** (0.46 g, 0.73 mmol) in toluene (20 mL) was treated with 1 N aqueous solution of NaOH (10 mL) for 1 h under nitrogen. The aqueous layer was separated and the solvent layer was dried on anhydrous sodium sulfate for 30 min. The deep blue color solution was obtained after filtration and the solvent was removed under vacuum. The resultant solid was recrystallized from a mixture of CH₂Cl₂/CH₃CN at -20 °C. Yield 0.20 g (47%). Anal. Calcd. for C₃₀H₅₃N₆OBCo: C, 61.8; H, 9.2; N, 14.4. Found: C, 61.6; H, 9.1; N, 14.3. IR (KBr cm⁻¹): ν(BH) 2552 ν(OH) 3670. UV–vis (toluene, nm, ε/M⁻¹ cm⁻¹): 532 (191), 667 (830). EI-MS (*m/z*): 566 [4-OH]. Magnetic moment (290 K): 4.48 B.M.

Preparation of [Co{HB(3-^tBu-5-ⁱPrpz)₃}]₂(CO₃) (**5**)

Under nitrogen, the complex **4** (0.20 g, 0.34 mmol) was dissolved in toluene (30 mL) in a Schlenk tube. The atmosphere in the tube was replaced with pure CO₂ and the solution was stirred at room temperature for 2 h. The solvent was then removed under vacuum and the resulting solid was recrystallized from CH₃CN/CH₂Cl₂ at -20 °C. Yield 0.20 g (49%). Anal. Calcd. for C₆₁H₁₀₄N₁₂O₃B₂Co₂: C, 61.4; H, 8.8; N, 14.1. Found: C, 60.7; H, 8.6; N, 13.9. IR (KBr cm⁻¹): ν(BH) 2566, ν(C=O) 1604. UV–vis (toluene, nm, ε/M⁻¹ cm⁻¹): 536 (371), 589 (649), 667 (1632). EI-MS (*m/z*): 1193 [Co{HB(3-^tBu-5-ⁱPrpz)₃}]₂(CO₃), 566 [Co{HB(3-^tBu-5-ⁱPrpz)₃}]⁺. Magnetic moment (290 K): 6.51 B.M.

Preparation of [Co{HB(3-^tBu-5-ⁱPrpz)₃}](OC₆H₄-*p*-NO₂) (**6**)

A solution of complex **4** (0.05 g, 0.09 mmol) in toluene (10 mL) was added to a stirred solution of sodium-4-nitrophenylacetate (0.02 g, 0.11 mmol) in toluene (10 mL). The mixture was stirred for 2 h. After removal of salt by filtration, the compound was dried under vacuum and recrystallized from CH₃CN at -20 °C. Yield 0.02 g (33%). Anal. Calcd. for C₃₆H₅₆N₇O₃BCo: C, 61.4; H, 8.0; N, 13.9. Found: C, 60.2; H, 7.9; N, 12.9. IR (KBr, cm⁻¹): ν(BH) 2569, ν(N=O) 1583, 1312. UV–vis (toluene, nm, ε/M⁻¹ cm⁻¹): 361 (7187), 608 (282), 671 (799). EI-MS (*m/z*): 704 [Co{HB(3-^tBu-5-ⁱPrpz)₃}](OC₆H₄-*p*-NO₂), 566 [Co{HB(3-^tBu-5-ⁱPrpz)₃}]⁺.

Preparation of [Co{HB(3,5-ⁱPrpz)₃}](OC₆H₄-*p*-NO₂)(CH₃CN)₂ (**7**)

To the solution of complex **2** (0.92 g, 0.85 mmol) in toluene (20 mL), the solution of 4-nitrophenyltrifluoroacetate

(0.2 g, 0.85 mmol) in toluene (15 mL), was added dropwise. The mixture was stirred for 6 h. Filtration and evaporation of solvent under vacuum resulted the red color compound which upon recrystallization from acetonitrile at 4 °C afforded the red color crystals suitable for X-ray data collection. Yield 0.31 g (65%). Anal. Calcd. for $C_{41}H_{62}N_{11}O_3BCo$: C, 62.93; H, 7.98; N, 21.2. Found: C, 60.20; H, 7.90; N, 12.85. IR (KBr, cm^{-1}): $\nu(BH)$ 2569, $\nu(CN)$ 2279, $\nu(N=O)$ 1583, 1312. UV–vis (toluene, nm, $\epsilon/M^{-1} cm^{-1}$): 570 (287), 730 (82).

X-ray data collections and structural determinations

Crystals suitable for X-ray analysis of **4** and **5** were obtained from CH_3CN/CH_2Cl_2 solutions and of **6** from CH_3CN at -20 °C. Single crystal of **2**, **5** · $3CH_2Cl_2$ · CH_3CN , and **6** · $2CH_3CN$ were coated with perfluoropolyether, picked up with glass fibers and mounted on a Siemens Smart-CCD diffractometer. Graphite

monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) was used throughout. Crystallographic data are listed in Table 1. Cell constants were obtained from a least squares fit of diffraction angles of several thousand strong reflections. Intensity data were corrected for Lorentz and polarization effects. Crystal faces were determined and the face-indexed correction routine embedded in SHELX TL [21, 22] was used to account for absorption. The SHELX TL software package was used for solution, refinement, and artwork of the structure. Non-hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Single crystal diffraction studies for **7** · $4CH_3CN$ was carried out on a Bruker Smart CCD diffractometer with Mo $K\alpha$ ($\lambda = 0.71073$ Å) sealed tube at 25 °C. Crystal structures were solved by direct methods and in anisotropic approximation refined using the SHELX TL package [21, 22]. Hydrogen atoms were constrained by rigid model. Complex **4** was found to be disordered on a crystallographic mirror plane. A split

Table 1 Crystal data and structure refinement for $[Co\{HB(3\text{-}^i\text{Bu-5-}^i\text{Prpz})_3\}(OH)]$ (**4**), $[Co\{HB(3\text{-}^i\text{Bu-5-}^i\text{Prpz})_3\}_2(CO_3)]$ (**5** · $3CH_2Cl_2$ · CH_3CN), $[Co\{HB(3\text{-}^i\text{Bu-5-}^i\text{Prpz})_3\}(OC_6H_4\text{-}pNO_2)]$ (**6** · $2CH_3CN$), $[Co\{HB(3,5\text{-}^i\text{Prpz})\}(OC_6H_4\text{-}pNO_2)(CH_3CN)_2]$ (**7** · $4CH_3CN$)

Complex	(4)	(5 · $3CH_2Cl_2$ · CH_3CN)	(6 · $2CH_3CN$)	(7 · $4CH_3CN$)
Empirical formula	$C_{30}H_{53}N_6OBCo$	$C_{66.3}H_{113.3}N_{13.30}O_3Cl_{5.40}B_2Co_2$	$C_{40}H_{62}N_9O_3BCo$	$C_{45}H_{68}N_{13}O_3BCo$
Formula weight	583.52	1,475.71	786.73	908.86
Temperature (K)	298(2)	298(2)	298(2)	298(2)
Wavelength (Å)	0.7107	0.7107	0.7107	0.7107
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	$Cmc2_1$	P-1	$P2_1/n$	$P2(1)$
Unit cell dimensions				
<i>a</i> (Å)	16.3208 (12)	9.8752 (4)	9.6256 (8)	11.702 (5)
<i>b</i> (Å)	10.2252 (8)	12.5748 (6)	25.199 (3)	12.478 (5)
<i>c</i> (Å)	19.669 (2)	17.3364 (8)	18.070 (2)	17.835 (7)
<i>V</i> (Å ³)	3,282.4 (5)	1,925.96 (15)	4,296.7 (8)	2,545.1 (18)
<i>Z</i>	4	1	4	2
ρ (calcd.) (mg m ⁻³)	1.181	1.272	1.216	1.186
μ (m ⁻¹)	0.554	0.669	0.446	0.387
<i>F</i> (000)	1,260	784	1,684	970
Crystal size (mm ³)	0.12 × 0.05 × 0.03	0.27 × 0.09 × 0.09	0.10 × 0.09 × 0.03	0.22 × 0.19 × 0.13
θ range for data collection (°)	3.9 to 27.5	3.23 to 31.0	3.25 to 21.0	1.17 to 25.5
<i>h</i> / <i>k</i> / <i>l</i> (max, min)	−22, 23/−14, 14/−28, 27	−14, 14/−18, 18/−23, 25	−9, 9/−25, 25/−17, 18	−14, 11/−15, 14/−22, 21
Reflection collected	3,754	12,206	4,591	9,197
Unique	2,908	8,597	3,218	7,875
Completeness (%)	96	99.4	99.5	97
Absorption correction	Gaussian	Gaussian	Gaussian	
Data/restraints/parameters	2,908/17/214	8,597/22/473	3,218/55/537	7,875/1/589
Goodness-of-fit on <i>F</i> ²	1.080	1.035	1.077	1.115
Final <i>R</i> ₁ , <i>wR</i> ₂ indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0518, 0.0823	0.0722, 0.1848	0.0635, 0.1435	0.0676, 0.1490
<i>R</i> ₁ , <i>wR</i> ₂ indices (all data)	0.0794, 0.0910	0.1103, 0.2125	0.1034, 0.1641	0.0809, 0.1697

model was applied to two *i*-propyl groups containing C6, C7, C8, and C26, C27, C28. The split positions were refined with equal occupation factors of 0.5, restrained C–C bond length, and equal anisotropic displacement parameters for corresponding split positions using SADI and EADP instructions of ShelXL. An electron density search around O1 suggested that the hydroxo proton is not exactly located on the crystallographic mirror plane. Its position (off the mirror plane) was therefore refined with an occupation factor of 0.5.

The bridging carbonate group in compound **5** is located on a crystallographic center of inversion and therefore leads to disorder. A test in acentric space group P1 (No.1) showed that the disorder still persists and therefore refinement in P-1 (No.2) is adequate. The occupation factors of the central carbon, C60, and of O1 were set to 0.5 but no further restrictions were applied. The refinement reveals that the carbonate anion binds in an asymmetrical fashion, bidentate to one cobalt and unidentate to the other. The compound contains dichloromethane and acetonitrile molecules of crystallization. One position was found to be occupied with both solvents and two split positions were refined with given total occupation factors of 0.5 each. To account for the disorder, positions of Cl3 and N90 were fixed to an identical position using EXYZ and anisotropically refined using the EADP instructions of ShelXL. Remaining atoms of the two solvents were isotropically refined since their positions are not well defined. Cl4 was further split on two sub positions with occupation of 0.25 each. C–Cl and Cl–Cl distances were restrained to be equal within errors using the SADI instruction.

All three isopropyl groups in complex **6** and an acetonitrile molecule of crystallization were found to be disordered over two sites. The isopropyl groups are disordered by rotation and therefore two split positions were refined for their methyl carbon positions. The disorder of the isopropyl groups leads to disorder of an acetonitrile molecule which was also split. The two resulting split parts were refined with an occupation ratio of about 0.61:0.39. SADI and EADP restraints were used.

Kinetics experiments for ester hydrolysis reaction in non-aqueous solution

Kinetic measurements for the hydrolysis of different esters were performed with a Lambda 35 Perkin Elmer UV–visible spectrophotometer by following the increases at the 360 nm absorption due to release of 4-nitrophenolate. The temperature was controlled at 25 °C in all experiments. Acetonitrile solution of esters (6.0 mM) and catalyst (**2/4**) (6.0 mM) were prepared as stock solution. The cell was prepared by taking ester (50.0 μ L), catalyst (500.0 μ L), and solvent acetonitrile (1,450 μ L). The absorption data

were recorded immediately after mixing the solution and followed until the formation of 4-nitrophenolate ion completed (means no change in the spectra was observed) [23]. Rate constants were calculated according to the published procedure [24, 25].

Results and discussion

Hydrolysis of esters

Structural determination of the mononuclear cobalt(II) hydroxo complex **4** prompted us to investigate the role of this complex and previously prepared binuclear cobalt(II) μ -hydroxo complex **2** in both carboxylate as well as phosphate esters hydrolysis. The ester hydrolysis was monitored spectrophotometrically. Figure 1 shows a representative example of the released 4-nitrophenolate at 360 nm for the reaction of **2**. The absorbance (A_t) at 360 nm was recorded at 5 min intervals over 60 min. The values of pseudo first order rate constants k were obtained from the slopes of the plots of $\text{Log}(A_{\text{int}} - A)$ versus time. Plots of k versus five different concentrations (1.5–5.25 mM) of **2/4** were linear confirming first order dependence on catalysts. The second order rate constant obtained according to $k = k_2 [\text{catalyst}]$. Figure 2 shows the plot of the k use for the hydrolysis of 4-nitrophenyltrifluoroacetate at various concentrations of **2**. Table 2 summarizes the first and second order rate constants for hydrolysis of esters obtained from the reaction of substrate and **2/4** complex in stoichiometric ratio. The results showed that both **2** and **4** can catalyze the hydrolysis

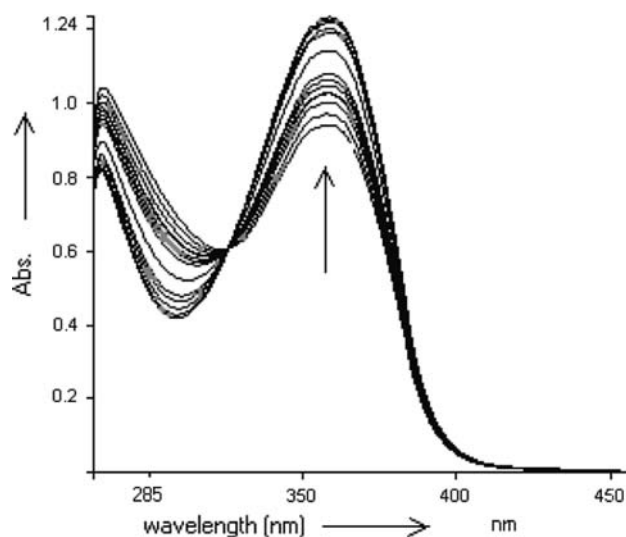


Fig. 1 A representative figure showing the increase in the absorbance of the released 4-nitrophenolate at 360 nm for the reaction of **2** (1.5 mM) with 4-nitrophenyl trifluoroacetate (0.15 mM) in CH_3CN at 300 K

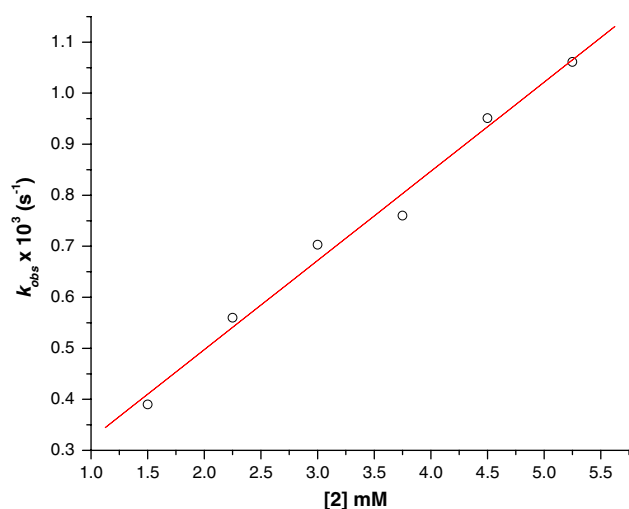


Fig. 2 Plot of the k values for the hydrolysis of 4-nitrophenyl trifluoroacetate at various concentrations of **2** in CH_3CN at 300 K

of phosphate as well as carboxylate ester. Like other researchers [26–28] we too observe that with Tp ligand system also, the hydrolysis of both phosphate as well as carboxylate ester is slower with catalyst **4** in comparison to **2**. The k_2 values obtained by **4** are smaller than that of **2**. Among the various ester taken in the present study, the k value is greater for 4-nitrophenyllaurate and lowest for 4-nitrophenylacetate with both **2** and **4**. This may be due to the fact that electron donating group present on ester facilitates the hydrolysis, whereas the electronic withdrawing group causes slow hydrolysis. A possible mechanism is shown in Scheme 1. Kinetic experiments indicated the dissociation of **2** to monomeric as nucleophile to attack the ester [29]. In the hydrolysis of both carboxylate as well as phosphate esters catalyzed by **2** and **4**, the carbonyl oxygen of the ester may be bound to the metal atom and the hydroxide ligand attacks the activated carbonyl group and then releases 4-nitrophenolate. The present findings may serve as model for cobalt(II) substituted zinc(II)-containing enzymes, viz., phosphatases [30].

We have also attempted the isolation and structural characterization of the ester hydrolysis products especially with 4-nitrophenyltrifluoroacetate (NPTFA) and 4-nitrophenylacetate (NPA) with complexes **2** and **4**, respectively.

Molecular structure of $[\text{Co}\{\text{HB}(3\text{-}^i\text{Bu}-5\text{-}^i\text{Prpz})_3\}(\text{OH})]$ (**4**)

The complex **4** was prepared by the reaction of a toluene solution of **3** with 1 N aqueous solution of NaOH (Scheme 2). Single crystals of **4** suitable for X-ray analysis were obtained by cooling the mixture of $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (50:50) solution to -20°C . Figure 3 shows a molecular structure of the **4**. The cobalt, oxygen, and one of the pyrazole rings (containing N22) sit on a crystallographic

mirror plane and this leads to two possible disordered positions for the hydrogen of the OH. The cobalt atom in complex **4** is in slightly distorted tetrahedral environment as evidenced by the three small N(pyrazole)–Co–N(pyrazole) bond angles (average, 93.7°) and coordinated by the N3O1 donor set. The Co–O distance is shorter than the averaged Co–N distance by 0.18 \AA . The average N(pyrazole)–Co–N(pyrazole) bond angle in **4** is larger than the N(pyrazole)–Co–N(pyrazole) bond angles (average 87.3°) in the square pyramidal cobalt complex **2** and also than in the recently reported five coordinate mononuclear hydroxo cobalt(II) complex with the N(pyrazole)–Co–N(pyrazole) bond angles (average 85.8°) [31, 32]. The average O–Co–N (pyrazole) bond angle (122.6°) in complex **4** is smaller than the average O–Co–N(pyrazole) bond angles (average 125.3°) present in **2**. The Co–O bond distance of $1.854(3) \text{ \AA}$ is slightly shorter than the Co–O bond distance in square pyramidal cobalt hydroxo complex [16]. Furthermore the evidence for the presence of the hydroxo group was provided by the appearance of $\nu(\text{OH})$ band at $3,670 \text{ cm}^{-1}$ in the IR spectrum of **4**. Thus, the complex **4** is mononuclear terminal hydroxo cobalt(II). To the best of our knowledge, this is the second example of a structurally characterized mononuclear tetrahedral cobalt (II) hydroxo complex [31, 32].

Molecular structure of $[\text{Co}\{\text{HB}(3\text{-}^i\text{Bu}-5\text{-}^i\text{Prpz})_3\}]_2(\text{CO}_3)]$ (**5**)

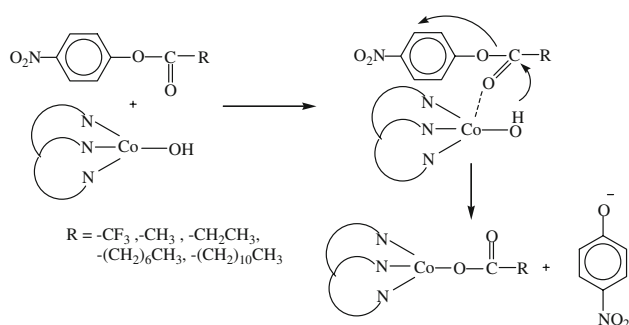
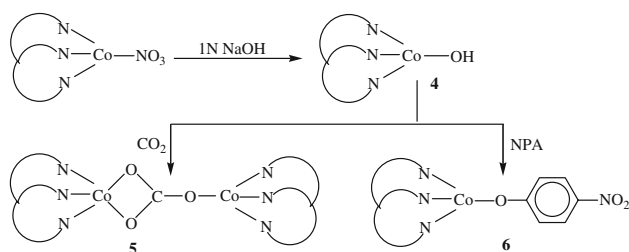
The reaction of **4** with carbon dioxide yielded complex **5**. When the toluene solution of **4** was exposed to 1 atm of CO_2 , pronounced color change from red to purple blue was observed (Scheme 2). Due to its low solubility, however, the crystallized product was (μ -carbonato) dicobalt complex **5** instead of mononuclear hydrogen carbonate complex $[\text{N}_3\text{Co}(\text{HCO}_3)]$. The crystal structure of the complex **5** was determined by X-ray crystallography and the molecular structure is given in Fig. 4. The selected bond lengths and bond angles are summarized in Table 3. As shown in Fig. 4, complex **5** has distorted structure. The bridging carbonate anion in complex **5** is bound in an unsymmetrical fashion; it coordinates to Co1 in a bidentate and to Co1A in unidentate fashion. Since the molecule resides on a crystallographic center of inversion, the carbonate anion is disordered but the two orientations could be resolved satisfactorily by a 50:50 split atom model.

¹ Hikichi et al. have reported the synthesis of mononuclear hydroxo complex with same ligand but never succeeded in getting crystal structure. They had also observed a peak due to product formed with CO_2 in mass spectral measurement.

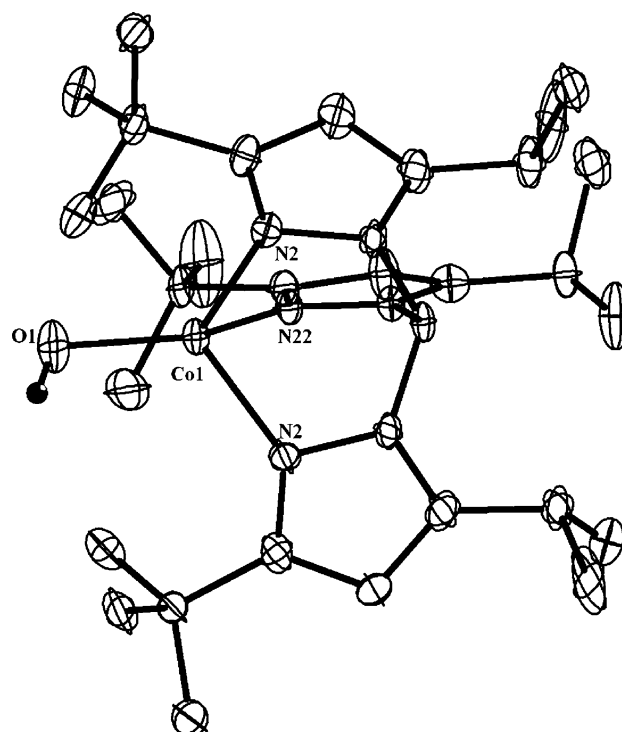
² See footnote 1.

Table 2 First and second order rate constants for hydrolysis of esters

Substrate	Hydroxo			
	Co ₂ (OH) ₂ {HB(3,5- ⁱ Prpz) ₃ } (2)		Co(OH){HB(3- ^t Bu-5- ⁱ Prpz) ₃ } (4)	
	<i>K</i> _{obs} (s ⁻¹)	<i>K</i> ₂ (M ⁻¹ s ⁻¹)	<i>K</i> _{obs} (s ⁻¹)	<i>K</i> ₂ (M ⁻¹ s ⁻¹)
4-Nitrophenyl trifluoro acetate	0.390 × 10 ⁻³	0.174	0.125 × 10 ⁻³	0.108
4-Nitrophenyl acetate	2.630 × 10 ⁻³	0.270	0.749 × 10 ⁻³	0.198
4-Nitrophenyl propionate	2.860 × 10 ⁻³	0.478	0.980 × 10 ⁻³	0.354
4-Nitrophenyl caprylate	3.640 × 10 ⁻³	0.402	1.267 × 10 ⁻³	0.287
4-Nitrophenyl laurate	4.361 × 10 ⁻³	0.757	1.502 × 10 ⁻³	0.352
Mono(4-nitrophenyl phosphate)	2.202 × 10 ⁻³	0.626	0.536 × 10 ⁻³	0.276
Bis(4-nitrophenyl phosphate)	1.060 × 10 ⁻³	0.513	0.337 × 10 ⁻³	0.212
Tris(4-nitrophenyl phosphate)	0.951 × 10 ⁻³	0.277	0.201 × 10 ⁻³	0.145

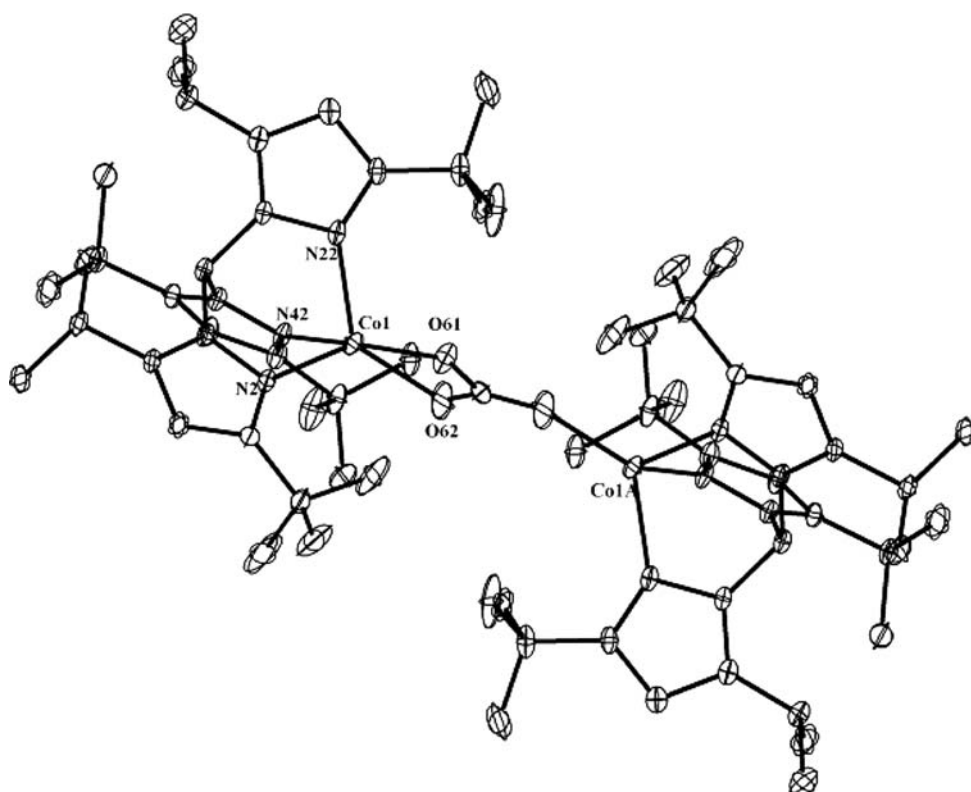
**Scheme 1** The proposed mechanism for the hydrolytic cleavage of different carboxylate esters using complex **2** as catalyst**Scheme 2** Synthesis of complexes **4**, **5** and **6**

The N₃O₂ ligand field around Co1 is much distorted because the distance between the cobalt and one oxygen from the carbonate is more elongated (Co1–O1, 2.151 (4) Å) than the other cobalt–oxygen bond distance (Co1–O2, 1.972 (3) Å). Similar type of coordination mode has been reported in literature by other workers also [16, 31,³ 32]. The Co–N bond lengths are almost equal (Co1–N2, 2.075(2); Co1–N40, 2.078(2); Co1–N21, 2.079(3) Å) but slightly longer than the reported zinc complex [16]. In complex **5**, one cobalt is five coordinate and other is four coordinate. Same type coordination environment was observed in [Zn(HB(3,5-ⁱPrpz)₃]₂(CO₃) [16] but not in

³ See footnote 1.**Fig. 3** Molecular structure of the Co{HB(3-^tBu-5-ⁱPrpz)₃} (OH) **4**

[Zn(HB(3-^tBu-5-Mepz)₃]₂(CO₃) where each zinc center is four coordinate [33, 34]. In [Co(HB(3,5-ⁱPrpz)₃]₂(CO₃) complex the coordination mode of CO₃ is completely different from that of **5** as in this complex, the carbonate group is coordinated to both cobalt ions in bidentate fashion. Accordingly, one of the Co–O1 bonds, where O1 denotes the oxygen atom of the carbonate group sitting between the two cobalt centers, is more elongated (ca. 2.27 Å) than the other (ca. 2.06 Å) and the bond distances between the cobalt and carbonate oxygens (O2 or O3) which are terminally bound to one side cobalt ion and are not equal: Co1–O2 (2.09 Å) vs Co2–O3 (1.99 Å). This is nice example of asymmetrical η₁η₂ coordination mode of a

Fig. 4 Molecular structure of $[\text{Co}\{\text{HB}(3\text{-}^i\text{Bu-}5\text{-}^i\text{Prpz})_3\}_2(\text{CO}_3)]$ (**5**)



carbonate group in a binuclear cobalt complex. The steric hindrance on Tp ligands as well as the nature of hydroxo (binuclear or mononuclear) complex seems to play an important role in deciding the coordination mode of CO_2 in its reaction product.

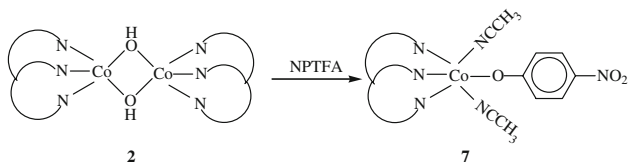
*Molecular structure of $[\text{Co}\{\text{HB}(3\text{-}^i\text{Bu-}5\text{-}^i\text{Prpz})_3\}(\text{OC}_6\text{H}_4\text{-}4\text{-NO}_2)]$ (**6**)*

Complex **6** was prepared by reaction of **4** and 4-nitrophenylacetate in 2:1 ratio in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ for 5 h (Scheme 2). Single crystals suitable for X-ray measurement were obtained by cooling of an acetonitrile solution to -20°C . Important bond lengths and angles are given in Table 3. As shown in Fig. 5, the cobalt atom is in pseudo-tetrahedral environment and is coordinated by the tridentate pyrazolylborate ligand and a monodentate 4-nitrophenolate anion. The Co1-O61 bond distance is

$1.890(5) \text{ \AA}$ which is slightly longer than the Zn-O bond distance ($1.860(2) \text{ \AA}$) in reported 4-nitrophenolate complex of zinc [35] and also than Co-O bond length in complex **4**. The Co-N bond distances in present complex are Co1-N42 ; $2.022(6)$, Co2-N(2) ; $2.024(5)$, and Co1-N22 ; $2.042(5) \text{ \AA}$ and are very similar to the Zn-N bond distances (Zn-N1 , $2.015(2)$; Zn-N2 , $2.024(2)$; Zn-N3 , $2.051(2) \text{ \AA}$) in zinc-nitrophenolate complex [35]. The Co1-O61-C62 bond angle ($151.3(3)^\circ$) is larger than Zn-O-C $132.6(2)^\circ$ in zinc-nitrophenolate [35].

*Molecular structure of $[\text{Co}\{\text{HB}(3,5\text{-}^i\text{Pr}_2\text{pz})_3\}(\text{OC}_6\text{H}_4\text{-}4\text{-NO}_2)(\text{CH}_3\text{CN})_2]$ (**7**)*

The reaction of **2** with 4-nitrophenyltrifluoroacetate (Scheme 3) resulted the formation of complex **7**. The structure of **7** was determined by X-ray crystallography and is given in Fig. 6. The cobalt(II) atom is octahedrally coordinated by the tripodal anionic pyrazolylborate ligand, a 4-nitrophenolate anion and two acetonitrile ligands bound in a cisoid fashion. The cobalt-nitrogen bond distances from the tris(pyrazolyl)borate ligand are (Co1-N1 , $2.147(4)$; Co1-N3 , $2.140(4)$; Co1-N5 , $2.144(5) \text{ \AA}$, which is longer than the Co-N bond distances in four coordinated cobalt-nitrophenolate complex having $\text{HB}(3\text{-}^i\text{Bu-}5\text{-}^i\text{Prpz})_3$ ligand. The Co-O bond distance (Co1-O1 , $2.016(4) \text{ \AA}$) which is again greater than Co-O bond distance (Co1-O1 ,



Scheme 3 Synthesis of complex **7**

Table 3 Selected bond distances (Å) and bond angles (°) for [Co{HB(3-^tBu-5-ⁱPrpz)₃}₂(OH)] (**4**), [Co{HB(3-^tBu-5-ⁱPrpz)₃}₂(CO₃)] (**5** · 3CH₂Cl₂ · CH₃CN), [Co{HB(3-^tBu-5-ⁱPrpz)₃}₂(OC₆H₄-4NO₂)] (**6** · 2CH₃CN), [Co{HB(3,5-ⁱPrpz)₃}₂(OC₆H₄-4NO₂)(CH₃CN)₂] (**7** · 4CH₃CN)

[Co{HB(3- ^t Bu-5- ⁱ Prpz) ₃ } ₂ (OH)] (4)			
Co(1)–O(1)	1.854(3)	O(1)–Co(1)–N(22)	123.8(2)
Co(1)–N(2)#1	2.042(3)	O(1)–Co(1)–N(2)#1	121.95(10)
Co(1)–N(22)	2.031(3)	N(22)–Co(1)–N(2)#1	93.50(10)
Co(1)–N(2)	2.042(3)	O(1)–Co(1)–N(2)	121.95(10)
		N(22)–Co(1)–N(2)	93.50(10)
		N(2) #1–Co(1)–N(2)	94.24(14)
[Co{HB(3- ^t Bu-5- ⁱ Prpz) ₃ } ₂ (CO ₃)] (5 · 3CH ₂ Cl ₂ · CH ₃ CN)			
Co(1)–O(62)	1.970(3)	O(62)–Co(1)–N(2)	125.63(11)
Co(1)–N(22)	2.078(2)	N(2)–Co(1)–N(22)	95.42(9)
Co(1)–O(61)	2.151(4)	O(62)–Co(1)–N(22)	131.98(11)
Co(1)–N(2)	2.075(2)	O(62)–Co(1)–N(42)	111.04(12)
Co(1)–N(42)	2.078(2)	N(2)–Co(1)–N(42)	90.24(9)
		N(22)–Co(1)–N(42)	90.11(9)
		O(62)–Co(1)–O(61)	56.29(15)
		N(2)–Co(1)–O(61)	100.93(14)
		N(22)–Co(1)–O(61)	96.11(14)
		N(42)–Co(1)–O(61)	166.60(13)
[Co{HB(3- ^t Bu-5- ⁱ Prpz) ₃ } ₂ (OC ₆ H ₄ -4NO ₂)] (6 · 2CH ₃ CN)			
Co(1)–O(61)	1.884(4)	O(61)–Co(1)–N(42)	134.00(17)
Co(1)–N(2)	2.026(4)	O(61)–Co(1)–N(2)	117.70(17)
Co(1)–N(42)	2.025(4)	N(42)–Co(1)–N(2)	95.93(16)
Co(1)–N(22)	2.041(4)	O(61)–Co(1)–N(22)	112.37(15)
		N(42)–Co(1)–N(22)	93.54(16)
		N(2)–Co(1)–N(22)	94.86(15)
[Co{HB(3,5- ⁱ Prpz) ₃ } ₂ (OC ₆ H ₄ -4NO ₂)(CH ₃ CN) ₂] (7 · 4CH ₃ CN)			
Co(1)–O(1)	2.016(4)	O(1)–Co(1)–N(3)	89.19(16)
Co(1)–N(5)	2.144(5)	O(1)–Co(1)–N(5)	176.45(17)
Co(1)–N(8)	2.181(4)	N(3)–Co(1)–N(5)	87.81(16)
Co(1)–N(3)	2.140(4)	O(1)–Co(1)–N(1)	91.85(16)
Co(1)–N(1)	2.147(4)	N(3)–Co(1)–N(1)	87.11(17)
Co(1)–N(7)	2.203(5)	N(5)–Co(1)–N(1)	86.09(16)
		O(1)–Co(1)–N(8)	89.11(16)
		N(3)–Co(1)–N(8)	177.5(2)
		N(5)–Co(1)–N(8)	93.95(17)
		N(1)–Co(1)–N(8)	94.79(18)
		N(3)–Co(1)–N(7)	90.81(17)
		N(1)–Co(1)–N(7)	175.16(18)
		N(5)–Co(1)–N(7)	89.47(15)
		O(1)–Co(1)–N(7)	92.49(16)
		N(8)–Co(1)–N(7)	87.41(18)

1.884(4) Å) in **6** and Zn–O bond distance (1.860 (2) Å) in 4-nitrophenolate complex of zinc [35]. The Co1–O1–C28, bond angle is 139.0(3)° which is smaller than the Co1–O61–C62 bond angle (151.3(3)°) in HB(3-^tBu-5-ⁱPrpz)₃

bonded cobalt-nitrophenolate complex but larger than Zn–O–C (132.6(2)°) in zinc-nitrophenolate [35].

Infrared spectra and magnetic properties of complexes

The IR spectrum of complex **3** shows two bands at 1,528 and 1,275 cm⁻¹ due to asymmetric and symmetric nitrate stretching. The presence of ν(OH) band at 3,670 cm⁻¹ in **4** suggested the coordination of hydroxo group which was confirmed in X-ray structure. Complex **5** exhibits a pronounced CO vibration at 1,604 cm⁻¹ indicating the possibility of CO₃²⁻ coordination to the metal center. In the IR spectrum of complexes **6** and **7**, the bands due to ν(N=O) appeared at 1,583 and 1,312 cm⁻¹ indicating the coordination of *p*-nitrophenolate as monodentate. The coordination of acetonitrile to the cobalt atom in **7** is supported by the presence of ν(CN) at 2,279 cm⁻¹. The temperature-dependent magnetic susceptibility measurement of complex **5** shows very weak antiferromagnetic coupling which is less than 2 cm⁻¹, and the magnetic moment of about 6.00 B.M. between 150 and 300 K is very similar to the magnetic behavior of other cobalt complexes [36, 37]. The fit and the dependence of the effective magnetic moment on temperature are displayed in Fig. S-1 of the supporting materials. The room temperature magnetic moment of **3** and **4** are 3.70 and 4.48 B.M., respectively.

Conclusions

In conclusion, we have reported the crystal structure of a mononuclear cobalt(II) hydroxo complex which is reactive toward CO₂ and esters. In general, a metal-bound hydroxo species is regarded as a nucleophile. The nucleophilicity of the hydroxo moiety in complexes **2** and **4** was investigated by kinetic experiments of 4-nitrophenylacetate hydrolysis along with other carboxylate and phosphate esters. The kinetic experiments indicated that the rate of generation of 4-nitrophenolate ion was varied from ester to ester and TpCoOH is the kinetically active species. The hydrolysis of ester occurs via a binuclear mechanism involving the nucleophilic attack of the metal-bound hydroxide to the carbonyl group of the ester as reported by other workers also [38–44]. The carbonic anhydrase also promotes the hydrolysis of 4-nitrophenylacetate [45] and follows second order kinetics, involving the direct nucleophilic attack at the carbonyl group by a Zn–OH species or hydroxo of other substituted metal ions. In order to get the model compound for CA, we also performed the reaction of complex **4** with CO₂, but due to poor solubility, the crystallized product was carbonato bridged **5** in place of mononuclear hydrogen carbonato complex.

Fig. 5 Molecular structure of $\text{Co}\{\text{HB}(3\text{-}^i\text{Bu-5-}^i\text{Prpz})_3\}(\text{OC}_6\text{H}_4\text{-p-NO}_2)$ **6**

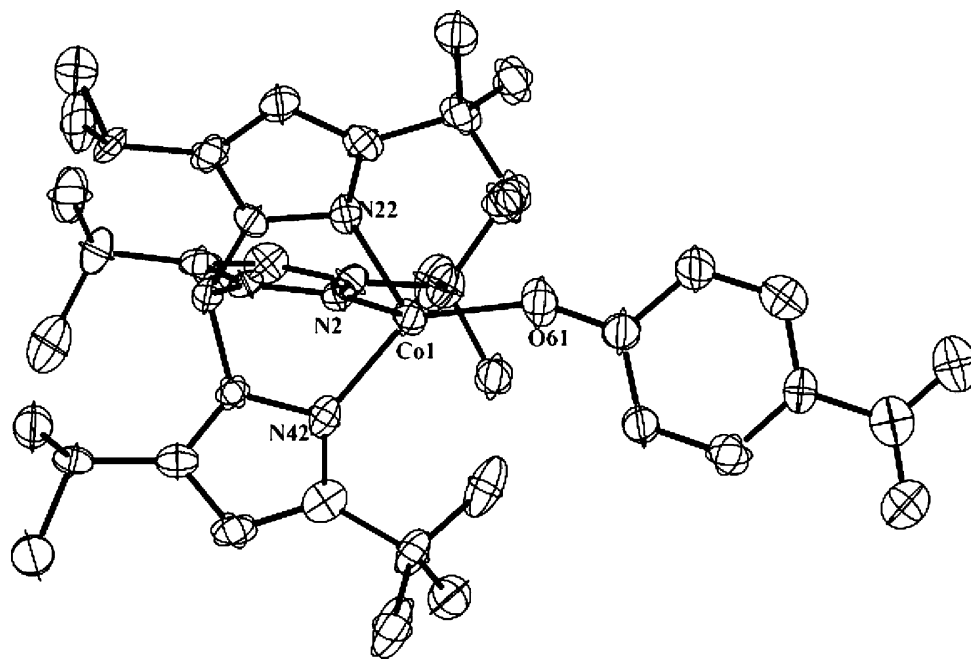
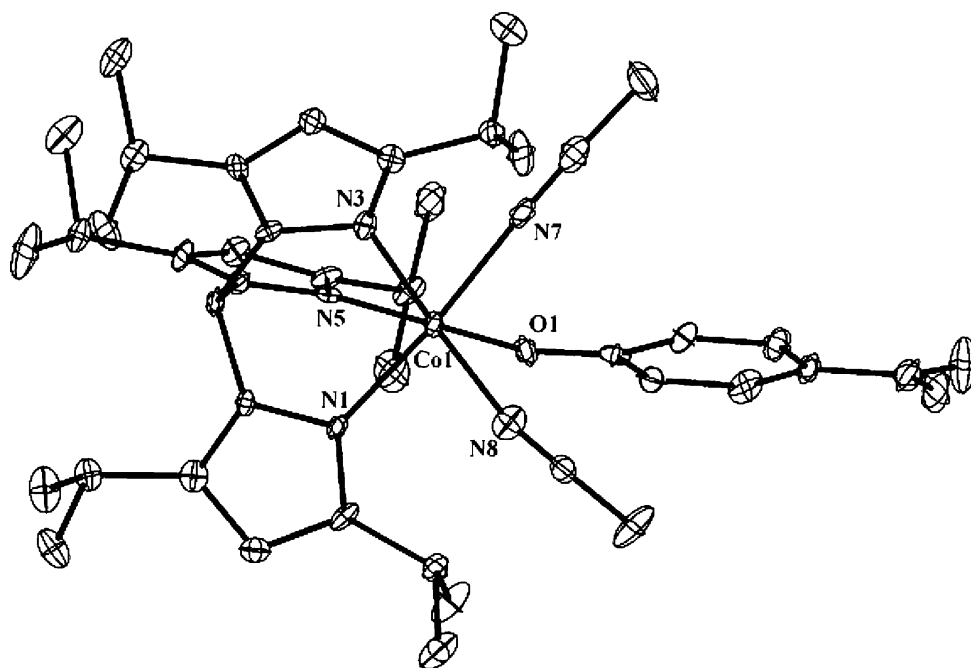


Fig. 6 Molecular structure of $\text{Co}\{\text{HB}(3,5\text{-}^i\text{Prpz})_3\}(\text{OC}_6\text{H}_4\text{-p-NO}_2)(\text{CH}_3\text{CN})_2$ **7**



Supplementary material

CCDC numbers 659652–659655 contain the supplementary crystallographic data (CIF) for this article. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments The authors are thankful to CSIR and AICTE, New Delhi, for the financial support in the form of research projects. UPS is grateful to the Alexander von Humboldt Foundation for

supporting the visit to Max-Planck-Institute für Bioanorganische Chemie, Mülheim, Germany, and Prof. K. Wieghardt for providing laboratory space and also for his continuous encouragement during my stay.

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