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Mononuclear cobalt(II) carboxylate complexes: Synthesis, molecular structure and selective oxygenation study

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Abstract

Some cobalt carboxylate (both mononuclear as well as binuclear) complexes have been prepared by using hindered hydrotris(3,5-diisopropyl-1-pyrazolyl)borate (Tp^{Pr2}) as supporting ligand. The reaction of $[Tp^{iPr2}Co(NO_3)]$ (**2**) with sodium benzoate resulted in the formation of acetonitrile coordinated complex $[Tp^{iPr2}Co(OBz)(CH_3CN)]$ (**3**) whereas the reaction of **2** with sodium fluorobenzoate gave coordinately unsaturated five coordinate complex of the type $[Tp^{iPr2}Co(F\text{-}OBz)]$ (**4**). The oxidation of compound **4** in the presence of 3,5-diisopropylpyrazole $3,5\text{-}Pr^i_2pzH$ resulted in the formation of a unique compound $[Co(F\text{-}OBz)\{HB(3\text{-}OCMe_2\text{-}5\text{-}Pr^ipz)(3,5\text{-}Pr^i_2pz)_2\}(3,5\text{-}Pr^i_2pzH)]$ (**5**) where only one methine carbon of isopropyl group on pyrazole ring of hydrotris(3,5-diisopropyl-1-pyrazolyl)borate oxidized and coordinated with cobalt center. In compound **5**, the binding behavior of fluorobenzoate also changes from bidentate to monodentate and the nonbonded oxygen atom formed intramolecular hydrogen bond with the hydrogen atom of the NH fragment of the coordinated $3,5\text{-}Pr^i_2pzH$. X-ray crystallography and IR studies confirmed the existence of hydrogen bonding in complex **5**. The pyrazolato bridged binuclear cobalt(II) complex $[(3,5\text{-}Pr^i_2pzH)_2Co_2(\mu\text{-}3,5\text{-}Pr^i_2pz)_2(NO_2\text{-}OBz)_2]$ (**6**) was prepared by the reaction of hydrated cobalt(II) nitrate, 3,5-diisopropylpyrazole and sodium nitrobenzoate where, each cobalt is four coordinate. The X-ray structure of **6** showed that the NH fragment of terminally coordinated $3,5\text{-}Pr^i_2pzH$ formed intramolecular hydrogen bonding with nonbonded oxygen atom of monodentately coordinated nitrobenzoate.

Keywords: Mononuclear complexes; Cobalt complexes; Monooxygenation; Intramolecular hydrogen bonding; Crystal structures

1. Introduction

The cobalt is an essential element for life although it does not participate in O_2 metabolism. Cobalt is found in vitamin B_{12}, that catalyzes trans-alkylation and isomerization via Co(III)-alkyl intermediate [1]. Besides vitamin B_{12}, there are several other cobalt containing proteins and enzymes [2–6] where cobalt is present in the active site or needed as cofactors for their functions. A common structural feature found in most of the cobalt-containing proteins and enzymes is the presence of one or more carboxylate groups derived from aspartate or glutamate side chains of the protein.

C–H bond functionalization by metal-coordinated active oxygen species is very interesting subjects from synthetic, catalytic, and bioinorganic point of view [7]. Various studies on C–H bond functionalization using metal–dioxygen complexes [8–12] revealed that a high valent metal–oxo (O^{2-}) species is formed via O–O bond cleavage of metal coordinated $O_2^{\,2-}$ species and work as an active intermediate for C–H bond oxygenation. Many examples of the ligand oxygenation including Tp^{iPr2} by using metal–oxo/peroxo complexes [11,12] have been reported in the literature. In general the aliphatic C–H bond oxygenation is rare [13–15] compared to aromatic oxygenation [16–18] and in all reported examples of aliphatic/aromatic C–H bond oxygenation, the source of oxygen is generally coordinated oxo/peroxo to metal center.

Coordination chemistry of metal carboxylato species is an attractive subject from the bioinorganic standpoint

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because the carboxylate group of glutamate and aspartate works as supporting ligand for the metal center in various metalloproteins and behave as monodentate or bidentate depending upon the requirement of active site. Accordingly, a variety of mononuclear carboxylate complexes with coordination number six are available in the literature [19,20]. But to the best of our knowledge, there are no examples available for five coordinated mononuclear cobalt carboxylate complexes. In present paper, we report the synthesis, structural characterization of mononuclear cobalt(II) benzoate, fluorobenzoate, binuclear pyrazolato bridged cobalt(II), and oxidation behavior of fluorobenzoate complex.

2. Experimental

2.1. Instrumentation

Carbon, hydrogen, and nitrogen were analyzed with a Vario EL III elemental analyzer after carefully dried samples under vacuum for several hours. IR spectra were obtained on a Thermo Nicolet Nexus FT-IR spectrometer in KBr. The UV–Vis spectra were recorded on Perkin–Elmer Lambda 35 UV/Vis spectrophotometer. FD-MS spectra were obtained on a Hitachi M-80 and FAB-MS spectra were obtained on VG Autospec mass spectrometer. The room temperature magnetic susceptibility measurements were done on a Princeton applied research vibrating sample magnetometer Model 155. The single crystal of **3** was coated with Fomblin® YR-1800, picked up with loop and mounted on a Siemens Smart-CCD diffractometer whereas the crystals of **4**–**6** were treated in same way but mounted on a Bruker Kappa Apex four circle-CCD diffractometer. Both systems were equipped with a nitrogen cold stream operating at 100 (±2) K. Graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) was used throughout. Crystal structures were solved by direct methods. Structure solution, refinement, and data output were carried out with the SHELXTL program [21,22]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions by using a riding model. Images were created with the DIAMOND program [23]. Hydrogen bonding interactions in the crystal lattice were calculated with SHELXTL and DIAMOND.

2.2. Materials and methods

All manipulations were carried out under nitrogen atmosphere by using standard Schlenk tube techniques unless otherwise stated. The required solvents were carefully purified and distilled under nitrogen prior to use by the literature method [24]. Cobalt(II) nitrate hexahydrate and sodium benzoate were of the highest grade commercially available and used without further purification. The *p*-X-benzoic acids (X = –F, –NO$_2$) were commercially available and their sodium salts were prepared by reacting with appropriate amount of sodium hydroxide in water. Potassium salt of hydrotris(3,5-diisopropyl-1-pyrazolyl)borate [HB(3,5-Pr$^i_2$pz)$_3$ = Tp^{iPr2}] (**1**) and [Tp^{iPr2}Co(NO$_3$)] (**2**) were synthesized by the literature methods [25,26].

2.3. [Tp^{iPr2}Co(OBz)(CH$_3$CN)] (**3**)

Compound **2** (0.29 g, 0.46 mmol) and sodium benzoate (0.07 g, 0.46 mmol) were stirred in a mixture of toluene and acetonitrile (1:1 ratio) for 12 h. The mixture was filtered over celite and solvent was evaporated to dryness under vacuum. The purple colored crystals in 73% yield (0.25 g, 0.36 mmol) were obtained by slow cooling of the acetonitrile solution at −20 °C. The elemental analysis was performed on vacuum dried sample for several hours. *Anal.* Calc. for C$_{36}$H$_{54}$N$_7$O$_2$BCo: C, 62.98; H, 7.93; N, 14.28. Found: C, 62.36; H, 7.70; N, 14.17%. IR (KBr, cm^{-1}): ν(BH) 2535, ν(CN) 2279, ν_{as}(COO) 1602, ν_s(COO) 1473. UV–Vis (toluene, nm, ε/M^{-1} cm^{-1}): 289 (1969), 574 (161). FD-MS (*m/z*): 645.

2.4. [Tp^{iPr2}Co(F-OBz)] (**4**)

To the toluene solution (15 ml) of **2** (0.51 g, 0.81 mmol) was added the acetonitrile solution (10 ml) of sodium *p*-fluorobenzoate (0.13 g, 0.81 mmol) drop-wise and the reaction mixture was stirred for 10 h. The resultant mixture was filtered over Celite and solvent was evaporated to dryness under vacuum. The compound was dissolved in a mixture of acetonitrile and dichloromethane solvent and the purple colored crystals were obtained at −20 °C in 52% yield (0.30 g, 0.45 mmol). *Anal.* Calc. for C$_{34}$H$_{50}$N$_6$O$_2$BFCo: C, 61.45; H, 7.58; N, 12.65. Found: C, 61.39; H, 7.82; N, 12.59%. IR (KBr, cm^{-1}): ν(BH) 2534, ν_{as}(COO) 1602, ν_s(COO) 1473. UV–Vis (toluene, nm, ε/M^{-1} cm^{-1}): 290 (1837), 576 (112). FAB-MS (*m/z*): 664. $\mu_{eff} = 3.89$ BM at 295 K.

2.5. [Co(F-OBz){HB(3-OCMe$_2$-5-Pr^i pz)(3,5-Pr$^i_2$pz)$_2$}(3,5-Pr$^i_2$pzH)] (**5**)

To dichloromethane solution (15 ml) of **4** (0.54 g, 0.70 mmol) was added 1 equiv. of 3,5-Pr$^i_2$pzH (0.11 g, 0.70 mmol) at room temperature and 30 equiv. of aqueous 30% H$_2$O$_2$ (2.15 ml, 21.0 mmol) drop-wise with continuous stirring. The reaction mixture was further stirred for one more hour. The reaction mixture was cooled at −20 °C for 10 min and filtered on Celite in cold condition. The solution was evaporated to dryness and the brown colored crystals were obtained from the mixture of acetonitrile and dichloromethane at −20 °C in 71% yield (0.59 g, 0.70 mmol). The elemental analysis was performed on vacuum dried sample for several hours. *Anal.* Calc. for C$_{43}$H$_{65}$N$_8$O$_3$BFCo: C, 62.24; H, 7.80; N, 13.54. Found: C, 61.89; H, 7.54; N, 13.31%. IR (KBr, cm^{-1}): ν(BH) 2541, ν_{as}(COO) 1607, ν_s(COO) 1467. UV–Vis (toluene, nm, ε/M^{-1} cm^{-1}): 284 (1837), 569 (112). $\mu_{eff} = 4.89$ BM at 295 K.

2.6. *$[(3,5\text{-Pr}^i_2\text{pzH})_2\text{Co}_2(\mu\text{-}3,5\text{-Pr}^i_2\text{pz})_2(\text{NO}_2\text{-OBz})_2]$ (6)*

$Co(NO_3)_2 \cdot 6H_2O$ (0.291 g, 1.0 mmol), $3,5\text{-Pr}^i_2\text{pzH}$ (0.302 g, 2.0 mmol) and sodium nitrobenzoate (0.189 g, 1.0 mmol) were stirred in a mixture of dichloromethane (20 ml) and acetonitrile (5 ml) for 8 h. The solution was filtered over Celite and the solvent was evaporated to dryness under vacuum. The violet colored crystals in 75% (0.79 g, 0.75 mmol) yield were obtained by slow cooling of acetonitrile solution at −20 °C. *Anal.* Calc. for $C_{50}H_{70}N_{10}O_8Co_2$: C, 56.81; H, 6.63; N, 13.25. Found: C, 56.51; H, 6.65; N, 13.10%. IR (KBr, cm^{-1}), $\nu_{as}(COO)$ 1591, $\nu_s(COO)$ 1471. $\mu_{eff} = 5.78$ BM per molecule at 295 K.

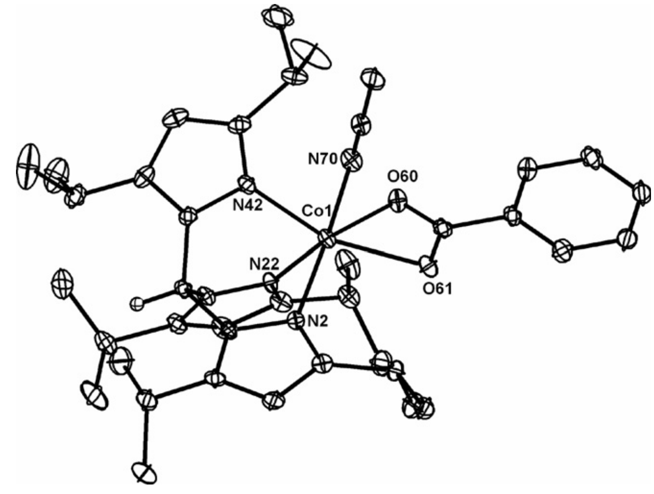


Fig. 1. Thermal ellipsoid view of $[Tp^{iPr2}Co(OBz) \cdot CH_3CN]$ (**3**) drawn at the 50% probability level. Hydrogen atoms and solvent molecule have been omitted for clarity.

3. Results and discussion

The previously prepared $[Tp^{iPr2}Co(NO_3)]$ (**2**) was used as starting material for the preparation of different benzoate complexes reported in the present paper. Complex **3** was prepared by the reaction of **2** with sodium benzoate. It was crystallized by slow cooling of acetonitrile solution at −20 °C and the structure was determined by X-ray crystallography. As shown in Fig. 1, the cobalt center has distorted octahedral geometry with N_4O_2 donor set having one coordinated acetonitrile at 6th position. The overall structure of the present octahedral complex is similar to one reported by the reaction of binuclear Co(II) hydroxo complex of Tp^{iPr2} with excess amount of benzoic acid [26]. The IR spectrum of **3** suggested the bidentate behavior of coordinated benzoate and was further supported by X-ray analysis. The Co–O bond lengths (Table 2) are very

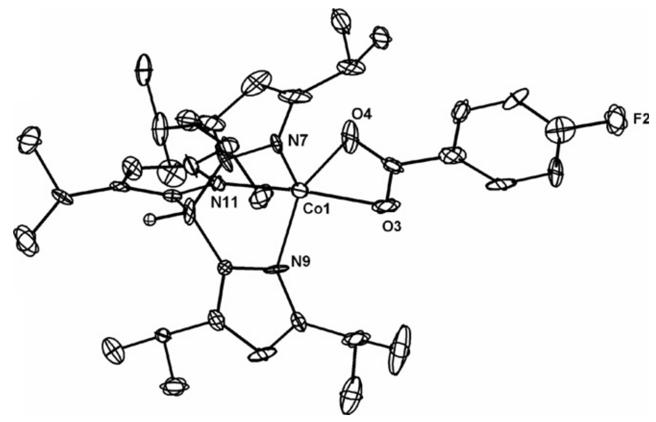


Fig. 2. Thermal ellipsoid view of $[Tp^{iPr2}Co(F\text{-}OBz)]$ (**4**) drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 1
Crystal data and data collection details of the complexes $[Tp^{iPr2}Co(OBz)(CH_3CN)]$ (**3**), $[Tp^{iPr2}Co(F\text{-}OBz)]$ (**4**), $[Co(F\text{-}OBz)\{HB(3\text{-}OCMe_2\text{-}5\text{-}Pr^i pz)(3,5\text{-}Pr^i_2pz)_2\}(3,5\text{-}Pr^i_2pzH)]$ ($\mathbf{5} \cdot CH_3CN \cdot CH_2Cl_2$), $[(3,5\text{-}Pr^i_2pzH)_2Co_2(\mu\text{-}3,5\text{-}Pr^i_2pz)_2(NO_2\text{-}OBz)_2]$ (**6**)

Complex	(**3**)	(**4**)	($\mathbf{5} \cdot CH_3CN \cdot CH_2Cl_2$)	(**6**)
Empirical formula	$C_{36}H_{54}N_7O_2BCo$	$C_{34}H_{50}N_6O_2FBCo$	$C_{89}H_{135}N_{17}O_6F_2B_2Cl_2Co_2$	$C_{50}H_{70}N_{10}O_8Co_2$
Formula weight	686.60	663.54	1787.52	1057.02
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions				
a (Å)	12.3935(4)	9.261(6)	14.026(9)	10.3603(8)
b (Å)	19.6719(8)	15.261(4)	18.810(10)	11.3682(8)
c (Å)	16.1545(6)	24.851(5)	21.645(14)	13.9441(10)
α (°)	90.00	90.361(3)	98.232(19)	67.8290(10)
β (°)	105.640(10)	95.020(4)	95.002(18)	70.8480(10)
γ (°)	90.00	90.911(5)	103.018(18)	88.5350(10)
V (Å^3)	3792.7(2)	3498(3)	5464(6)	1427.61(18)
Z	4	4	2	1
D_{calc} (g/cm^3)	1.202	1.260	1.086	1.229
Data collection				
$2\theta_{max}$ (°)	60.0	51.00	51.62	54.8
Number of measured reflections	31027	13030	21050	10775
Number of observed reflections	10972	6829	5128	5272
Number of parameters refined	437	819	1058	324
R	0.0408	0.0461	0.0838	0.0410
R_w	0.0838	0.1022	0.2192	0.1131

similar to the metal–oxygen bond in previously reported mononuclear benzoate complexes of cobalt(II) [26] and manganese(II) [27], but are slightly shorter than the Fe–O bond distance in a six-coordinate iron(II)–benzoate complex [16] (Fig. 2).

Attempts were made to prepare the oxygen sensitive cobalt(II) compound so that the oxidation/oxygenation studies could be performed. The reaction of complex **2** with sodium fluorobenzoate in acetonitrile–toluene solution resulted in the formation of five coordinated [Tp^{iPr2}Co(F-OBz)] (**4**) whose IR clearly indicated that the fluorobenzoate is coordinated in bidentate manner. The suitable crystal for X-ray data collection was obtained by slow cooling of the acetonitrile–dichloromethane solution of **4** at −20 °C. The crystallographic data of **4** are listed in Table 1 and important bond lengths and bond angles are given in Table 2. As shown in Fig. 3, the metal center of **4** is in five coordination atmosphere coordinated with three nitrogen atom from Tp^{iPr2} ligand and two oxygen atoms from the fluorobenzoate. The Co–O bond lengths (Table 2) are similar to that in complex **3**, whereas the Co–N bond distances are slightly smaller than the Co–N bond distances in **3**. On the basis of X-ray data, it may be presumed that the geometry around metal center may be square pyramidal. As per our effort toward the oxygen activation by transition metal complexes, a toluene solution of **4** was exposed to dioxygen at room temperature but no color change was observed even after cooling the solution at −50 °C. Since complex **4** is five coordinate, coordinatively unsaturated, it was thought that it could be oxidized by suitable oxidizing agents. To our surprise, during the oxidation of **4** with H_2O_2, in the presence of 1 equiv. of free 3,5-diisopropylpyrazole, we got the monooxygenated intramolecular hydrogen bonded cobalt(II) complex **5** (Scheme 1). In complex **5**, one of the six methine groups in the isopropyl substituents of Tp^{iPr2} distal to the metal center is oxidized in place of metal and resulted in the six coordinated intramolecular hydrogen bonded fluorobenzoate complex. As shown in Fig. 3, the coordination behavior of fluorobenzoate changed from bidentate to monodentate. The Co1–O1 bond distance of the coordinated oxygen is 1.951(8) Å, whereas the Co1–O2 bond distance is 3.474 Å. The long distance of Co1–O2 bond indicated that this oxygen was not involved in coordination with metal center. The cobalt–nitrogen bond distances of coordinated Tp^{iPr2} are in the range of 1.851(8)–2.010(9) Å, which are shorter than metal–nitrogen bond distances in **4**. The nonbonded oxygen atom of fluorobenzoate formed intramolecular hydrogen bond with NH group of 3,5-Pr$^i_2$pzH. The existence of hydrogen bonding in complex **5** has been established on the basis of the absence of νN–H band of free pyrazole (which appear at 3180 cm^{-1} in free 3,5-Pr$^i_2$pzH) as well as the location of hydrogen atom in X-ray structure with bond distance of N8–Ha, 0.861 Å; O2-Ha, 1.921 Å. The bond distance between nitrogen of free pyrazole and the nonbonded oxygen atom of fluorobenzoate is 2.752 Å (N8–O2). These distances are well within the range of hydrogen bonding as reported in the literature for other metal complexes [27,28]. The formation of monooxygenated cobalt(II) complex is not unusual in the oxidation chemistry of Tp^{iPr2} coordinated cobalt(II) compound as reported by Hikichi et al. [12]. They have reported the extensive studies on aliphatic C–H oxygenation by Co(II)-peroxo species [12] and

Table 2
Selected bond distances (Å) and bond angles (°) for [Tp^{iPr2}Co(OBz)(CH$_3$CN)] (**3**), [Tp^{iPr2}Co(F-OBz)] (**4**), [Co(F-OBz){HB(3-OCMe$_2$-5-Pr^{i}pz)(3,5-Pr$^i_2$pz)$_2$}(3,5-Pr$^i_2$pzH)] (**5** · CH$_3$CN · CH$_2$Cl$_2$), [(3,5-Pr$^i_2$pzH)$_2$Co$_2$(μ-3,5-Pr$^i_2$pz)$_2$(NO$_2$-OBz)$_2$] (**6**)

[Tp^{iPr2}Co(OBz)(CH$_3$CN)] (**3**)			
Bond lengths (Å)			
Co(1)–N(2)	2.160(12)	Co(1)–N(22)	2.051(12)
Co(1)–N(42)	2.088(12)	Co(1)–N(70)	2.211(13)
Co(1)–O(60)	2.105(10)	Co(1)–O(61)	2.174(11)
Bond angles (°)			
N(2)–Co(1)–N(70)	173.35(5)	N(22)–Co(1)–N(70)	89.59(5)
N(22)–Co(1)–O(60)	170.74(4)	N(22)–Co(1)–O(61)	108.83(4)
N(42)–Co(1)–O(60)	97.98(4)	N(42)–Co(1)–O(61)	158.69(4)
O(60)–Co(1)–N(2)	98.04(4)	O(60)–Co(1)–N(70)	88.55(4)
O(61)–Co(1)–N(70)	82.77(5)		
[Tp^{iPr2}Co(F-OBz)] (**4**)			
Bond lengths (Å)			
Co(1)–N(7)	2.039(8)	Co(1)–N(9)	2.103(9)
Co(1)–N(11)	2.042(9)	Co(1)–O(3)	2.011(7)
Co(1)–O(4)	2.184(7)		
Bond angles (°)			
N(7)–Co(1)–N(9)	91.0(4)	N(11)–Co(1)–N(7)	90.6(4)
N(11)–Co(1)–N(9)	90.0(4)	N(7)–Co(1)–O(4)	111.1(4)
N(9)–Co(1)–O(4)	154.4(4)	N(11)–Co(1)–O(4)	102.1(4)
O(3)–Co(1)–N(7)	114.4(4)	O(3)–Co(1)–N(11)	153.5(4)
O(3)–Co(1)–N(9)	97.7(5)	O(3)–Co(1)–O(4)	62.0(3)
[Co(F-OBz){HB(3-OCMe$_2$-5-Pr^{i}pz)(3,5-Pr$^i_2$pz)$_2$}(3,5-Pr$^i_2$pzH)] (**5** · CH$_3$CN · CH$_2$Cl$_2$)			
Bond lengths (Å)			
Co(1)–N(1)	1.984(9)	Co(1)–N(3)	2.010(9)
Co(1)–N(5)	1.851(8)	Co(1)–N(7)	1.985(10)
Co(1)–O(1)	1.951(8)		
Bond angles (°)			
N(1)–Co(1)–N(3)	87.9(4)	N(1)–Co(1)–N(7)	173.4(5)
N(5)–Co(1)–N(1)	84.0(4)	N(5)–Co(1)–N(3)	96.2(5)
N(5)–Co(1)–N(7)	90.4(4)	N(7)–Co(1)–N(3)	89.2(4)
N(5)–Co(1)–O(1)	171.6(3)	N(5)–Co(1)–O(3)	81.7(4)
O(1)–Co(1)–N(1)	89.4(4)	O(1)–Co(1)–N(3)	88.7(4)
O(1)–Co(1)–N(7)	96.4(4)	O(3)–Co(1)–N(1)	94.1(4)
O(3)–Co(1)–N(3)	176.9(3)	O(3)–Co(1)–N(7)	88.5(4)
O(3)–Co(1)–O(1)	93.7(3)		
[(3,5-Pr$^i_2$pzH)$_2$Co$_2$(μ-3,5-Pr$^i_2$pz)$_2$(NO$_2$-OBz)$_2$] (**6**)			
Bond lengths (Å)			
Co(1)–N(2)	2.004(17)	Co(1)–N(4)	1.986(16)
Co(1)–N(5)	1.987(16)	Co(1)–O(1)	1.943(15)
N(4)–N(5)	1.375(2)	O(3)–N(1)	1.204(4)
O(4)–N(1)	1.220(4)		
Bond angles (°)			
N(4)–Co(1)–N(2)	107.60(7)	N(4)–Co(1)–N(5)	111.67(7)
N(5)–Co(1)–N(2)	106.84(7)	O(1)–Co(1)–N(2)	114.68(7)
O(1)–Co(1)–N(4)	109.24(7)	O(1)–Co(1)–N(5)	106.86(7)

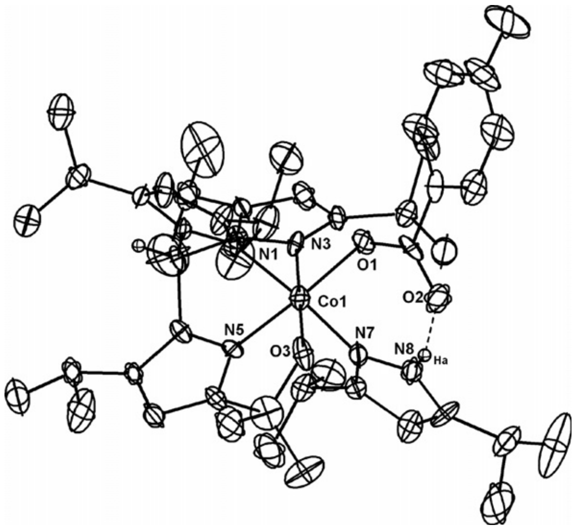


Fig. 3. Thermal ellipsoid view of [Co(F-OBz){HB(3-OCMe$_2$-5-Pr^{i}pz)(3,5-Pr$^i_2$pz)$_2$}(3,5-Pr$^i_2$pzH)] (**5** · CH$_3$CN · CH$_2$Cl$_2$) drawn at the 30% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity.

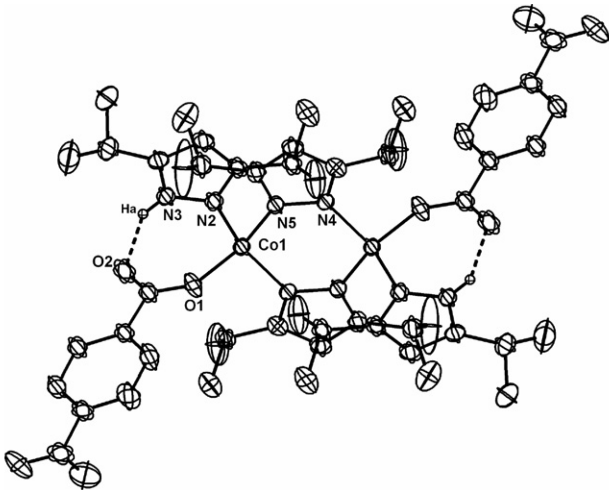
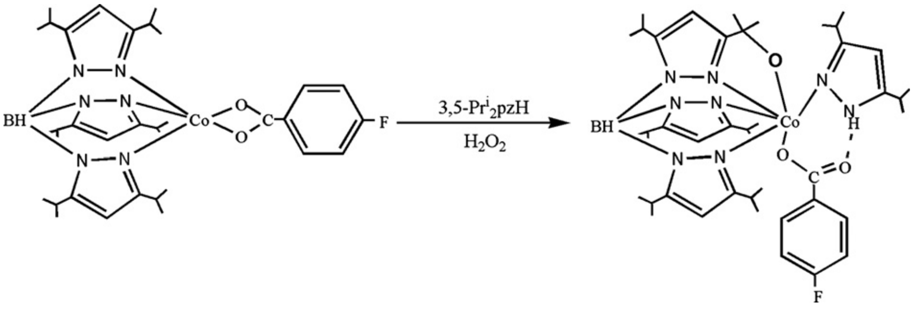


Fig. 4. Thermal ellipsoid view of [(3,5-*i*Pr$^i_2$pzH)$_2$Co$_2$(μ-3,5-Pr$^i_2$pz)$_2$(NO$_2$-OBz)$_2$] (**6**) drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

demonstrated the formation of binuclear mono-oxygenated, di-oxygenated, and mononuclear fully oxygenated Co(II) complex. In all these complexes, the metal center is five coordinated and no hydrogen bonding exits. In present mono-oxygenated Co(II) complex **5**, the metal center is six coordinate and intramolecular hydrogen bonding exits. To our knowledge this is first example of monooxygenated Co(II) six coordinate mononuclear complex with intramolecular hydrogen bonding.

In other set of experiment, when a mixture of cobalt (II) nitrate, 3,5-diisopropylpyrazole, and sodium nitrobenzoate was allowed to react for 6 h, a binuclear compound of the type [(3,5-Pr$^i_2$pzH)$_2$Co$_2$(μ-3,5-Pr$^i_2$pz)$_2$(NO$_2$-OBz)$_2$] (**6**) was isolated. The suitable single crystal for X-ray data collection was obtained from acetonitrile solution at −20 °C. A thermal ellipsoidal view of complex **6**, representing a novel di(μ-pyrazolato)dicobalt core, is depicted in Fig. 4. The selected bond lengths and bond angles are summarized in Table 2. Cobalt–nitrogen bond distances of both bridging pyrazolato are same (Table 2) whereas the cobalt–nitrogen bond distance for terminally coordinated pyrazole are slightly longer (Co1–N2, 2.004(17) Å) than the bridging ones. As shown in X-ray structure, both nitrobenzoate groups are coordinated unidentately with cobalt metal ions. The uncoordinated oxygen atom of both nitrobenzoates form hydrogen bond with the hydrogen atom (NH fragment) of 3,5-Pr$^i_2$pzH. The nitrogen–oxygen bond distance of 2.771 Å (N3–O2), (N3–Ha, 0.860 Å; O2–Ha, 2.002 Å) clearly indicates the presence of hydrogen bonding in complex **6**. The Co–Co separation in this complex is 3.597 Å, which is longer than the Co–Co separation in binuclear cobalt complexes having Tp$^{i\mathrm{Pr}2}$ ligand [12,26,29] but shorter than the recently reported similar binuclear cobalt(II) complex with Co–Co distance of 3.629 Å [30]. The cobalt atoms are bridged via the N atoms of two bridging pyrazolate ligands produced through deprotonation of the 3,5-Pr$^i_2$pzH molecules. Each cobalt is coordinated by the one nitrogen atom of the terminal pyrazole molecule and oxygen atom of the terminal nitrobenzoate anion. Compound **6** appears to be an unusual binuclear complex in which each cobalt(II) atom is electron deficient (15 electrons) and is in a distorted tetrahedral environment.



Scheme 1. Stick figure diagram for oxidation reaction.

4. Conclusion

$[\mathrm{Tp}^{i\mathrm{Pr}2}\mathrm{Co(OBz)(CH_3CN)}]$ complex **3** was obtained by the reaction of $[\mathrm{Tp}^{i\mathrm{Pr}2}\mathrm{Co(NO_3)}]$ (**2**) and sodium benzoate. The X-ray studies demonstrated the presence of six coordinated metal center in complex **3** due to the coordination of acetonitrile at vacant 6th position of the cobalt center. On the other hand, the reaction of **2** with sodium fluorobenzoate gave five coordinate complex **4** which is coordinatively unsaturate with three nitrogen atoms from $\mathrm{Tp}^{i\mathrm{Pr}2}$ ligand and two oxygen atoms from fluorobenzoate. Complex **4** was oxidized with 30% H_2O_2 in the presence of free pyrazole. The oxidized product **5** has a unique structure. In complex **5**, the cobalt is still in two oxidation state, one of the six methine carbon atoms in the isopropyl groups of $\mathrm{Tp}^{i\mathrm{Pr}2}$ ligand is oxygenated and form bond with cobalt center. The coordination behavior of fluorobenzoate is changed from bidentate to monodentate. The one oxygen atom of monodentately coordinated fluorobenzote forms intramolecluar hydrogen bond with NH fragment of the coordinated $3,5\text{-}\mathrm{Pr}^i_2\mathrm{pzH}$ giving six coordination number to the cobalt center. The formation of pyrazolato bridged binuclear cobalt(II) complex **6** indicated that the coordinated 3,5-diisopropylpyrazole molecule can behave in both protonated as well as deprotonated form in same compound. In complex **6**, the deprotonated $3,5\text{-}\mathrm{Pr}^i_2\mathrm{pzH}$ bridges between two cobalt centers and protonated $3,5\text{-}\mathrm{Pr}^i_2\mathrm{pzH}$ form intramolecular hydrogen bonds. This may help in understanding the mechanism of the action of metalloenzymes, where the imidazole fragment of the terminal histidine molecule is present in their active site [31] and the binuclear metal carboxylate complexes serve as models [32].

5. Supplementary material

CCDC 637433, 637434, 637435, and 637436 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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