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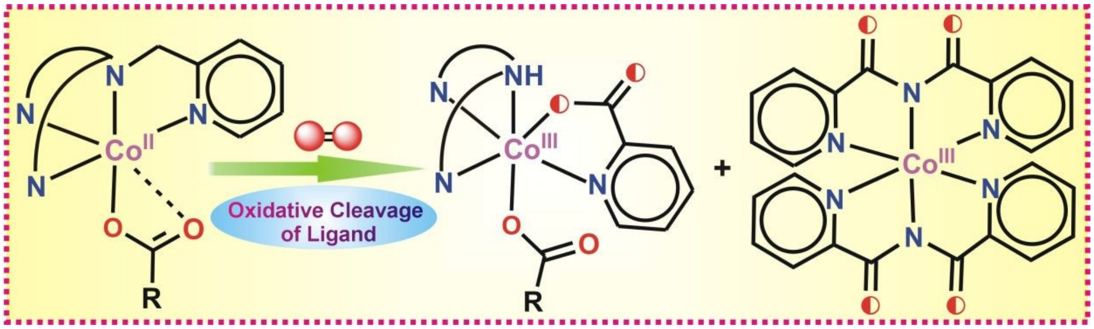

Cobalt(II)-carboxylate complexes of N4 ligands containing (2-pyridylmethyl)amine backbone activate dioxygen to carry out the oxidative C-N bond cleavage of the ligand. The coordination of carboxylate co-ligand plays important role to carry out the ligand oxidation.

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Oxidative C-N Bond Cleavage of (2-Pyridylmethyl)amine-Based Tetradentate Supporting Ligands in Ternary Cobalt(II)-Carboxylate Complexes

Biswarup Chakraborty,[#] Ivy Ghosh,[#] Rahul Dev Jana, and Tapan Kanti Paine*

Three mononuclear cobalt(II)-carboxylate complexes, $[(TPA)Co^{II}(benzilate)]^+$ (**1**), $[(TPA)Co^{II}(benzoate)]^+$ (**2**) and $[(iso\text{-}BPMEN)Co^{II}(benzoate)]^+$ (**3**) of N4 ligands (TPA = tris(2-pyridylmethyl)amine, *iso*-BPMEN = *N*^{1},*N*^{1}-dimethyl-*N*^{2},*N*^{2}-bis((pyridin-2-yl)methyl)ethane-1,2-diamine) were isolated to investigate their reactivity toward dioxygen. Monodentate (η^1) binding of the carboxylates to the metal centre favours the five-coordinate cobalt(II) complexes (**1**-**3**) for dioxygen activation. Complex **1** slowly reacts with dioxygen to exhibit oxidative decarboxylation of the coordinated α-hydroxy acid (benzilate). A prolonged exposure of the reaction solution of **2** to dioxygen results in the formation of $[(DPA)Co^{III}(picolinate)(benzoate)]^+$ (**4**) and $[Co^{III}(BPCA)_2]^+$ (**5**) (DPA = di(2-picolyl)amine and HBPCA = bis(2-pyridylcarbonyl)amide), whereas only $[(DPEA)Co^{III}(picolinate)(benzoate)]^+$ (**6**) (DPEA = *N*^{1},*N*^{1}-dimethyl-*N*^{2}-(pyridine-2-ylmethyl)-ethane-1,2-diamine) is isolated from the final oxidised solution of **3**. The modified ligand DPA (or DPEA) is formed via oxidative C-N bond cleavage of the supporting ligands. Further oxidation of the $–CH_2–$ moiety to –C(=O)- takes place in the transformation the DPA to HBPCA on cobalt(II) centre. Labelling experiments with $^{18}O_2$ confirm the incorporation of oxygen atoms from molecular oxygen into the oxidised products. Mixed labelling studies with $^{16}O_2$ and H_2O^{18} strongly support the involvement of water in the C-N bond cleavage pathway. A comparison of the dioxygen reactivity of the cobalt complexes (**1**-**3**) with several other five-coordinate mononuclear complexes $[(TPA)Co^{II}(X)]^+$, (X = Cl, CH_3CN, acetate, benzoylformate, salicylate and phenylpyruvate) establishes the role of carboxylate co-ligands in the activation of dioxygen and subsequent oxidative cleavage of the supporting ligands by a metal-oxygen oxidant.

Introduction

Tripodal tetradentate nitrogen ligands[1-3] have received considerable attention in studies related to dioxygen activation at metal centre and to stabilise metal ions in unusual oxidation states.[4-11] Transition metal complexes of nitrogen rich (2-pyridylmethyl)amine-based ligands are used extensively as catalysts for a variety of oxidation reactions.[12-16] In the catalytic pathway, metal based oxidants have been proposed to affect the oxidation reactions. These ligands contain reactive C-H bonds and are unstable under oxidising conditions. As a result, many of these ligands suffer oxidative degradation in catalytic reactions.[17, 18] Oxidative ligand hydroxylation by C-H activation has been reported with metal complexes of nitrogen donor ligands containing active methylene groups.[19-21] Unusual reactivity of the $-CH_2-$ groups with metal complexes of tripodal (2-pyridylmethyl)amine-type ligands has been documented.[10, 17, 22-25]

The stability of cobalt-oxygen species makes cobalt complexes as ideal candidates to get information about O_2-derived intermediates in enzymatic reactions.[26] Cobalt (II) complexes of tripodal nitrogen donor ligands containing reactive methylene groups [27-29] have been reported to activate dioxygen to form different cobalt-oxygen adducts.[30-38] We have investigated the dioxygen reactivity of cobalt(II) complexes of (2-pyridylmethyl)amine-derived ligands with an objective to gain insights into the nature of intermediate generated in the reductive activation of dioxygen by analogous iron(II)-α-hydroxy acid complexes.[39] During the course of this investigation, a new mode of reactivity of the cobalt(II) complexes was observed. The cobalt(II)-α-hydroxy acid complex, $[(TPA)Co^{II}(benzilate)]^+$ (**1**) (TPA = tris(2-pyridylmethyl)amine) exhibits oxidative decarboxylation of benzilate in the reaction with dioxygen similar to that observed with the corresponding iron(II)-benzilate complex. On the contrary, the cobalt(II)-carboxylate complexes $[(TPA)Co^{II}(benzoate)]^+$ (**2**) and $[(iso\text{-}BPMEN)Co^{II}(benzoate)]^+$ **(3)** (*iso*-BPMEN = *N*^{1},*N*^{1}-dimethyl-*N*^{2},*N*^{2}-bis((pyridin-2-

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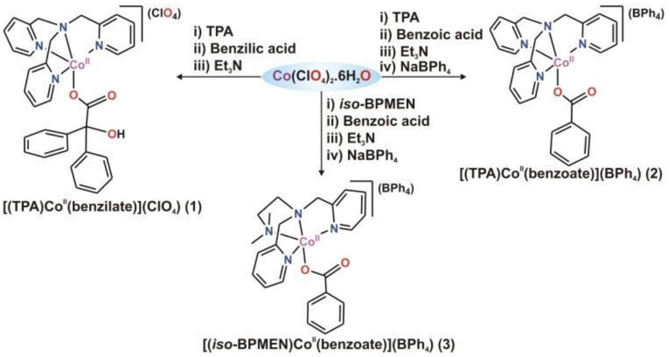
yl)methyl)ethane-1,2-diamine) undergo oxidative C-N bond cleavage/oxygenation of the supporting N4 ligands. The role of oxygen and water during the oxidative reactions is established by labelling experiments. The influence of a carboxylate co-ligand on the reactivity of cobalt(II) complexes is discussed in this work and compared with those of a series of previously reported cobalt(II) complexes of the same supporting ligand.



Scheme 1 Five-coordinate cobalt(II)-carboxylate complexes of N4 ligands.

Results and discussion

Synthesis and characterization

The cobalt(II) complexes were isolated from the reactions of equimolar amounts of the tetradentate ligand, cobalt(II) perchlorate hydrate, carboxylic acid (benzilic acid or benzoic acid) and triethylamine (Experimental Section). The complexes were isolated as either perchlorate or tetraphenylborate salts. The FT-IR spectra of the complexes show sharp bands in the regions 1627-1604 cm^{-1} and 1367-1339 cm^{-1} attributable to ν_a(COO) and ν_s(COO), respectively. The energy difference $\Delta\nu$(COO) of >200 cm^{-1} is consistent with the monodentate binding mode of the carboxylate groups.[40] The ESI-mass spectra of the complexes show molecular ion peaks at *m/z* 575.38, 470.10, and 450.25 with the isotope distribution patterns calculated for [(TPA)Co(benzilate)]$^+$, [(TPA)Co(benzoate)]$^+$ and [(*iso*-BPMEN)Co(benzoate)]$^+$, respectively. All the cobalt(II) complexes exhibit broad and paramagnetically shifted ^{1}H NMR spectra in solution typical of high-spin cobalt(II) complexes (Figure S1, supporting Information, SI). The room temperature magnetic moment values of the complexes are found in the range of 4.06-4.32 μ_B. A large orbital contribution of the metal ion results in higher magnetic moments than calculated for the spin-only value of high-spin d^7 system. The magnetic moment values and the ^{1}H NMR spectra unambiguously support the high-spin nature of the mononuclear cobalt(II) complexes.

The cobalt(II)-carboxylate complexes display three ligand field transitions in the visible region (460-650 nm) with low molar extinction coefficients (Fig. S2), typical of high-spin cobalt(II) complexes.[41-43] Moreover, the energies of these bands are very similar to those observed in five-coordinate high-spin cobalt(II) complexes Co(Et$_4$-dien)X$_2$ (X = Br, NCS, N$_3$) in solution. The bands originate from the spin-allowed transitions from the microstates of two ^{4}F and ^{4}P ground state terms of Co(II) in C$_{3v}$ symmetry.[44, 45] The composition of the cobalt(II)-carboxylate complex **2** in solution was further verified by optical titration of [(TPA)Co^{II}(CH$_3$CN)](ClO$_4$)$_2$ [46] with benzoate in acetonitrile at 25°C. With incremental addition of benzoate, three new bands at 461 nm, 607 nm and 624 nm appear whereas the band at 552 nm slowly disappears (Fig. 1). No spectral change is observed after addition of 0.9 equiv. of benzoate. The spectral changes clearly suggest the coordination of carboxylate to the metal-ligand complex with the formation of about 90% complex in solution. The final spectrum matches perfectly with that of an acetonitrile solution of **2**.

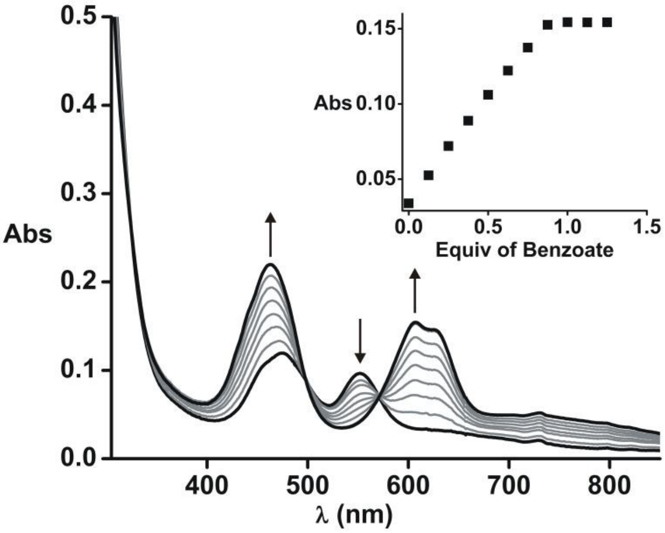


Fig. 1 Optical spectral changes upon addition of a mixture of benzoic acid and triethylamine into a solution of [(TPA)Co^{II}(CH$_3$CN)]$^{2+}$ in acetonitrile (1 mM) at 298 K.

Structure of Co(II)-carboxylate complexes

X-ray structures of **1** and **2** (Table S1) reveal that in each of the monomeric cobalt complexes, the metal centre is ligated by four nitrogen donors from the neutral tetradentate ligand and one carboxylate oxygen (O1) of the monoanionic carboxylate (benzilate for **1** and benzoate for **2**) resulting in distorted trigonal bipyramidal (TBP) coordination geometry (Fig. 2). The axial positions of the distorted TBP geometry are occupied by the amine nitrogen N3 of TPA and the carboxylate oxygen (O1) with the N3–Co1–O1 angles of 167.40(11)° and 170.10(7)° for **1** and **2**, respectively (Table 1). The equatorial positions are occupied by three pyridine nitrogens (N1, N2 and N4) of the supporting ligand. The Co-N bond distances are observed in the range of 2.0605(19)–2.2109(18) Å similar to that observed in reported five-coordinate high-spin cobalt(II) complexes.[41-43] Several attempts to isolate single crystals of complex **3** failed. However, DFT optimisation of **3** indicates a five-coordinate geometry with monodentate carboxylate being energetically more favourable than the six-coordinate complex (Fig. S3 and Table S2). Furthermore, the bond parameters (Table S2) of the five-coordinate geometry of **3** match well with those of the structurally characterised complexes **1** and **2**.

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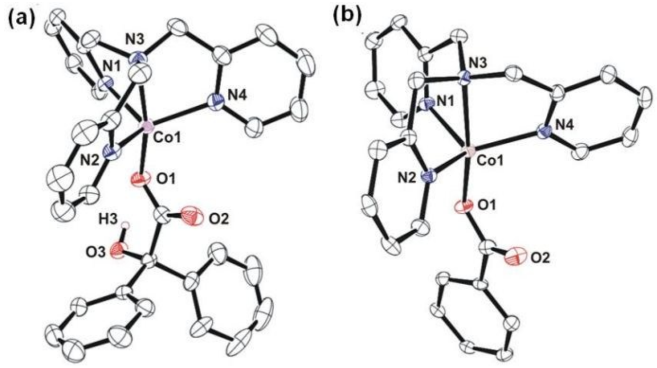

Fig. 2 ORTEP plots of the complex cations of (a) **1** and (b) **2** with 30% thermal ellipsoid parameters. The counter ions have been omitted for clarity.

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

Bond distances/angles	**Complex 1**	**Complex 2**
Co(1)–O(1)	1.985(3)	1.9680(15)
Co(1)–N(1)	2.089(3)	2.0809(19)
Co(1)–N(2)	2.088(3)	2.0648(18)
Co(1)–N(3)	2.195(3)	2.2109(18)
Co(1)–N(4)	2.087(3)	2.0605(19)
O(1)–Co(1)–N(1)	92.18(11)	93.23(7)
O(1)–Co(1)–N(2)	103.56(12)	105.76(7)
O(1)–Co(1)–N(3)	167.40(11)	170.10(7)
O(1)–Co(1)–N(4)	112.90(12)	108.40(7)
N(1)–Co(1)–N(2)	114.43(12)	113.26(7)
N(1)–Co(1)–N(3)	76.44(12)	76.96(7)
N(1)–Co(1)–N(4)	113.45(12)	115.36(7)
N(2)–Co(1)–N(3)	76.92(12)	77.45(7)
N(2)–Co(1)–N(4)	117.05(12)	117.34(7)
N(3)–Co(1)–N(4)	77.18(12)	77.53(7)

Between the two N4 ligands, the *iso*-BPMEN ligand with one flexible arm (-CH_2-CH_2-NMe_2) allows more distortion at the cobalt centre (τ = 0.64) in **3** compared to **1** and **2** (*τ* values around 0.88). Of note, almost ideal TBP geometries (*τ*; 0.96-0.99) are observed for $[(TPA)Co^{II}Cl]^+$ and $[(TPA)Co^{II}CH_3CN]^{2+}$ complexes.[43, 46] However, cobalt(II) centre in the five-coordinate complexes (**1-3**) and in the previously reported complexes ($[(TPA)Co^{II}Cl]^+$, $[(TPA)Co^{II}CH_3CN]^{2+}$, $[(TPA)Co^{II}(salicylate)]^+$, $[(TPA)Co^{II}(benzoylformate)]^+$, and $[($*iso*-$BPMEN)Co^{II}(salicylate)]^+$) is situated 0.39-0.47 Å below the equatorial plane formed by three nitrogen donors (N1-N2-N4) of the ligands (Fig. 3).

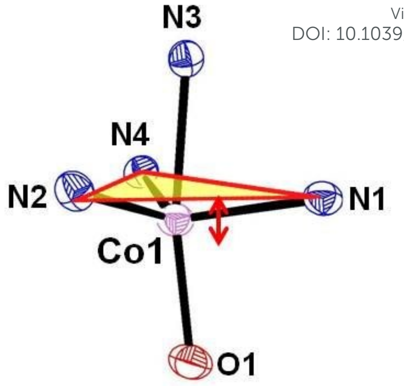

Fig. 3 Five-coordinate TBP geometry at the cobalt centre of cobalt(II)-complexes where the central atom is situated below the equatorial plane (yellow triangle formed by N1, N2 and N4 atoms, whereas the red arrow indicates the distance of the Co(II) atom from the plane).

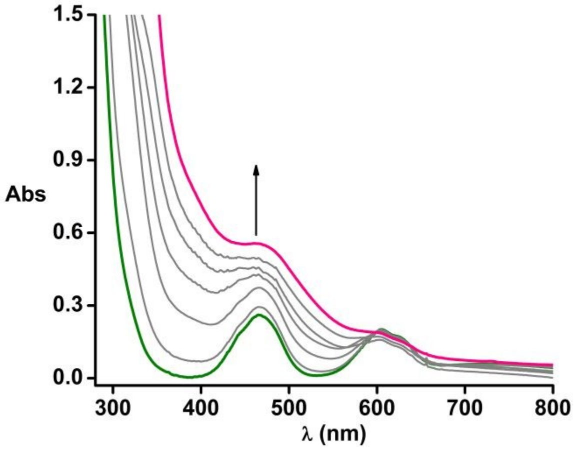

Fig. 4 Optical spectral change of **1** (1mM in acetonitrile) during the reaction with dioxygen at 298 K.

Reaction of the Co(II) complexes with dioxygen

The cobalt(II) complexes are stable in the solid state and in solution under inert atmosphere but are air-sensitive in solution. Complex **1** in acetonitrile reacts with oxygen over a time period of one week during which the d-d bands slowly disappear with concomitant formation of a broad band with absorption maxima at 470 nm (Fig. 4). The ^1H NMR signals in the downfield region vanishes with time with the appearance of three new signals at 7.8 ppm, 7.6 ppm and 7.5 ppm. The ^1H NMR spectrum of the oxidised solution suggest the formation of a low-spin cobalt(III) species (Figs. 5 and S5). The three signals in diamagnetic region are attributed to the aromatic protons of non-coordinated benzophenone. Other peaks in the aromatic region originate from the protons of pyridine rings of the TPA ligand. The ESI-mass spectrum of the oxidised solution of **1** shows an ion peak at *m/z* 349.22 calculated for $[(TPA)Co]^+$ (Fig. S4). Therefore, oxidative transformation of the metal-bound benzilate to benzophenone takes place in the reaction with dioxygen. A control experiment with an equimolar mixture of cobalt(II) perchlorate hexahydrate, benzilic acid and Et_3N in acetonitrile does not yield any decarboxylated product. Thus the oxidative decarboxylation of benzilate by the cobalt

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complex is similar to that reported for iron(II)-benzilate complexes of tridentate and tetradentate nitrogen ligands.[39, 47-49]

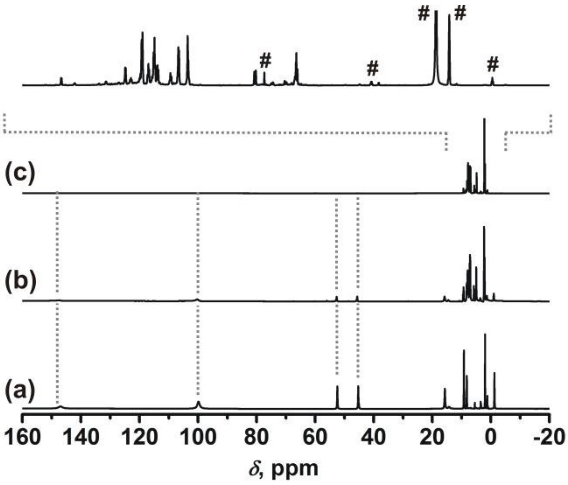

Fig. 5 ^1H NMR spectral (500 MHz, CD_3CN, 298 K) changes with time ((a) 0 h (b) 3 d (c) 1 week) during the reaction of **1** with dioxygen. The peaks marked as # originate from residual CH_3CN and H_2O in NMR solvent, and traces of CH_3OH added to improve the solubility of the complex.

Complex **2** in acetonitrile also reacts with dioxygen at 298 K. The d-d bands disappear over a period of 3 weeks with the formation of a broad band showing absorption at 470 nm (Fig. S6a). In the ESI-mass spectrum of the oxidised solution of **2,** ion peaks at *m/z* 256.01, 379.05 and 511.02 with the isotope distribution patterns calculated for $[(DPA\text{-}H_2)Co]^+$, $[(DPA\text{-}H)Co(picolinate)]^+$ and $[(BPCA)_2Co]^+$, (DPA = di(2-picolyl)amine and HBPCA = bis(2-pyridylcarbonyl)amide) respectively, are detected (Fig. 6). The results suggest the formation of at least two cobalt(III) complexes of DPA and BPCA ligands after the oxidation of **2** (Scheme 2).

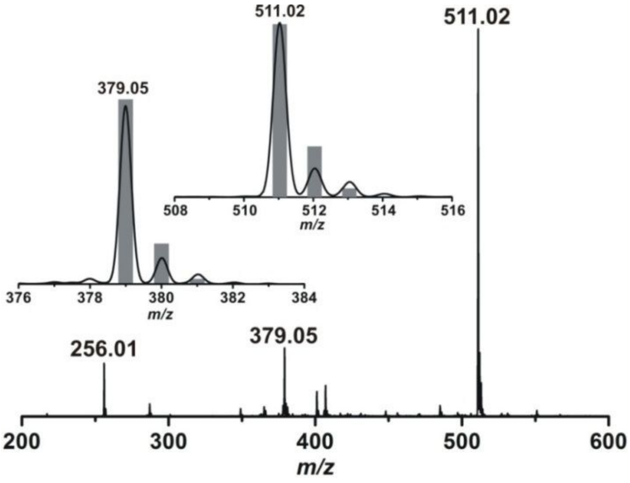

Fig. 6 ESI-mass spectrum (positive ion mode in acetonitrile) of the oxidised solution of **2.**

A red crystalline solid of one of the complex $[(DPA)Co(picolinate)(benzoate)](ClO_4)$ (**4**) was isolated from the oxidised solution of **2** after three weeks. The ^1H NMR spectrum of the crystalline solid exhibits signals between 4 ppm and 12.5 ppm typical of a low-spin cobalt(III) complex (Fig. 7). The resonance of -NH_{amine} proton of DPA is shifted down-field to 12.2 ppm and appears as a broad singlet. A sharp singlet for one of the protons of picolinate unit is observed at 9.8 ppm. The α-protons of the pyridine rings of DPA appear as a doublet at 8.4 ppm. Other aromatic protons are observed between 7 ppm and 8 ppm. Two multiplet signals of the aliphatic **-**CH_2 protons of DPA appear at around 5 ppm.

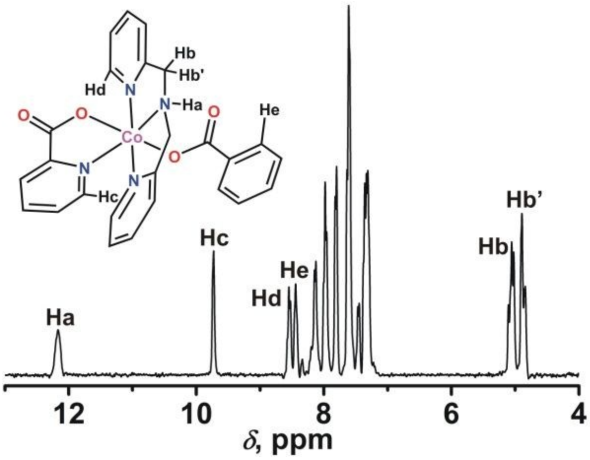

Fig. 7 ^1H NMR (300 MHz, CD_3CN, 298K) spectrum of $[(DPA)Co(picolinate)(benzoate)](ClO_4)$ (**4**).

The X-ray crystal structure of **4** (Table S3) shows a monomeric six-coordinate cobalt centre ligated by three nitrogen donors of di-2-picolylamine (DPA), one carboxylate oxygen (O1) of benzoate and, one carboxylate oxygen (O3) and the pyridine nitrogen (N4) of picolinate (Fig. 8). The axial positions of the distorted octahedron are occupied by the carboxylate oxygens (O1 and O3) with the O1-Co1-O3 angle of 173.90(12)° whereas the equatorial plane is composed of the nitrogen donors N1, N2, N3 and N4. The metal-ligand bond distances (Table S4) are found in the range between 1.904(3) Å and 1.939(4) Å, typical of low-spin cobalt(III) complexes. An intramolecular hydrogen bonding interaction is observed between the amine nitrogen (N2) of DPA and the carboxylate oxygen atom O2 of benzoate with the N2···O2 distance of 2.736 Å.

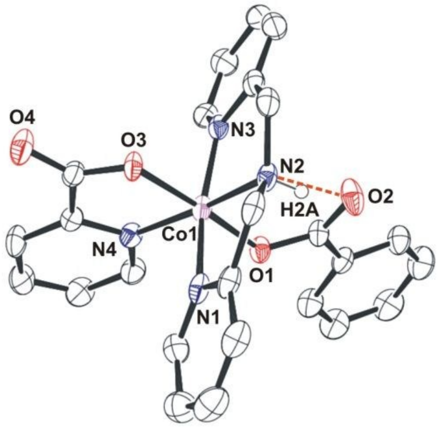

Fig. 8 ORTEP plot of the cationic part of **4** with 30% ellipsoid probability. Counter anion, solvent molecules and hydrogen atoms except H2A are

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omitted for clarity. Red dotted line represents the intramolecular hydrogen bonding interaction.

Crystalline solid of another cobalt(III) complex, $[(BPCA)_2Co](BPh_4)$ (**5**) was isolated from the oxidised solution of **2** in the presence of sodium tetraphenylborate. The ^1H NMR spectrum of **5** displays resonance signals between 6.5 ppm and 8.5 ppm (Fig. S7). Two doublet signals and two triplet signals are observed above 7.5 ppm attributable to the aromatic protons of the pyridine rings of BPCA ligand. The integration patterns of the peaks indicate the presence of a four-fold symmetry in the cationic part of the complex in solution. X-ray crystal structure of the cationic complex displays a mononuclear six-coordinate cobalt centre coordinated by two monoanionic BPCA (Fig. S8). The cationic part of **5** is *iso*-structural with the reported complex $[Co^{III}(BPCA)_2](ClO_4)$ with comparable bond parameters (Table S5).[50]

The cobalt(II)-benzoate complex (**3**) of the *iso*-BPMEN ligand upon prolonged exposure to dioxygen in acetonitrile results in a broad band at 475 nm (Fig. S6b). The ESI-mass spectrum of the oxidised solution exhibits ion peaks at *m/z* 359.09 and 481.13 along with the isotope distribution patterns attributable to $[(DPEA\text{-}H)Co(picolinate)]^+$ and $[(DPEA)Co(picolinate)(benzoate)]^+$ (where DPEA = N^1,N^1-dimethyl-N^2-((pyridin-2-yl)methyl)ethane-1,2-diamine) (Fig. S9). In the ^1H NMR spectrum, the proton resonances are observed in the region between 2.5 ppm and 12.5 ppm suggesting the diamagnetic nature of the cobalt species. The ^1H NMR (Fig. 9) and ESI-mass spectra of the red solid isolated from the oxidised solution of **3** confirms the formation of a cobalt(III) complex with the molecular formula $[(DPEA)Co^{III}(picolinate)(benzoate)](BPh_4)$ (**6**) as the only species. Herein, picolinate is exclusively formed upon oxidative C-N bond cleavage of one of the pyridylmethyl arm of the *iso*-BPMEN ligand. Thus the C-N bond of the aliphatic arm ($-CH_2-CH_2-NMe_2$) is less reactive than that of the pyridylmethyl arm ($-CH_2-Py$).

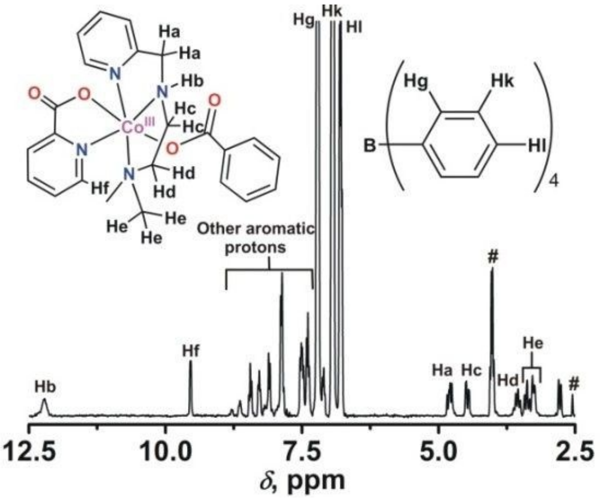


Fig. 9 ^1H NMR spectrum (500 MHz, CD_3CN, 298 K) of $[(DPEA)Co^{III}(picolinate)(benzoate)](BPh_4)$ (**6**).

Effect of carboxylate co-ligand

Although all the three cobalt(II) complexes have five-coordinate geometry, their reaction towards dioxygen is controlled by the axial ligand present at the fifth coordination site. Complex **1** undergoes oxidative decarboxylation of the axial co-ligand benzilate to benzophenone, whereas the reactions of complexes **2** and **3** (with benzoate as co-ligand) with dioxygen lead to the oxidative C-N cleavage of the ligand backbone. In the ligand oxidation pathway, one of the pyridylmethyl arms of the TPA/*iso*-BPMEN is oxidatively cleaved to form the modified ligands DPA, DPEA, BPCA and picolinate (Scheme 2). In addition, the dioxygen reactivity of two other five-coordinate cobalt(II) complexes $[(TPA)Co^{II}(Cl)](ClO_4)$ and $[(TPA)Co^{II}(CH_3CN)](ClO_4)_2$ that lack any carboxylate donor was also investigated. We reported two biomimetic cobalt(II)-α-keto acid complexes $[(TPA)Co^{II}(BF)](BPh_4)$ and $[(TPA)Co^{II}(PPH)](BPh_4)$ (BF = benzoylformate an PPH = phenylpyruvate). The reaction of $[(TPA)Co^{II}(PPH)](BPh_4)$ with dioxygen affords $[(TPA)Co^{III}(PP)](BPh_4)$, whereas $[(TPA)Co^{II}(benzoate)]^+$ is formed upon oxidative decarboxylation of $[(TPA)Co^{II}(BF)](BPh_4)$ over the course of 5 days.[41] A prolonged exposure of $[(TPA)Co^{II}(BF)]^+$ to dioxygen also forms a mixture of $[(DPA)Co^{III}(picolinate)(benzoate)]^+$ and $[Co^{III}(BPCA)_2]^+$ (Fig. S10). The cobalt(II)-acetate complex $[(TPA)Co^{II}(acetate)](BPh_4)$[51] displays similar reactivity as observed with $[(TPA)Co^{II}(benzoate)](BPh_4)$ (Fig. S11). On the other hand, the cobalt(II)-chloro complex $[(TPA)Co^{II}(Cl)](ClO_4)_2$ is stable in air and does not react with dioxygen but the cobalt(II)-acetonitrile complex $[(TPA)Co^{II}(CH_3CN)](ClO_4)_2$ forms a dimeric cobalt(III)-hydroxo complex $[(TPA)Co^{III}(OH)](ClO_4)_2\}_2$ (**7**).

X-ray crystal structure of **7** (Table S3) reveals a hydroxo-bridged dimeric cobalt(II) complex, where the two metal ions are separated by 2.9591(15) Å (Fig. 10). Each of the metal ion in **7** is in distorted octahedral coordination geometry with four nitrogen donors from ligand and two oxygen atoms of the bridging hydroxo ligands. The axial positions are occupied by a hydroxo oxygen (O1′) and a pyridine nitrogen (N3) with the O1′-Co1-N3 angle of 177.75(18)°. The Co-N distances in the range 1.915(5)–1.932(4) Å are typical of cobalt(III) complexes (Table S6).

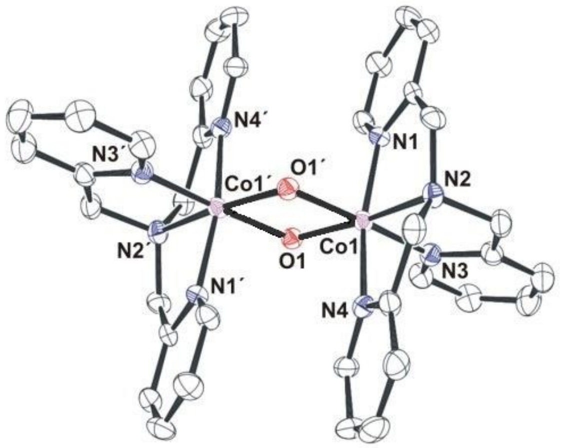
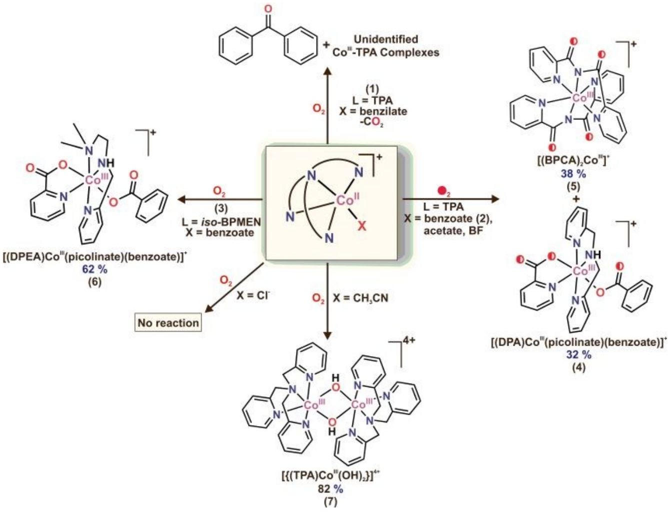


Fig. 10 ORTEP plot of **7** with 40% ellipsoid probability. Counter anions and hydrogen atoms are omitted for clarity. Symmetry code (′): *½-x, ½-y, z*.

From the results described above, it is clear that the oxidation of the methylene groups of TPA (and of *iso*-BPMEN) is associated with the dioxygen activation at the metal centre and can only be observed when one carboxylate co-ligand is coordinated. The products, formed upon ligand cleavage, remain coordinated to the metal centre in the oxidised complexes **4** and **5**. The ESI-mass spectrum of the oxidised solution of **2** after the reaction with dioxygen in the presence of excess benzilic acid (20 equiv) and triethylamine shows ion peak at *m/z* 349.09 for $[(TPA)Co]^+$ (Fig. S12). Thus, the oxidative cleavage of a ligand arm can be avoided in the presence of excess amount of substrate such as benzilate, which does not form carboxylate ligand upon oxidation.



Scheme 2 Reactions of the five-coordinate cobalt(II) complexes of TPA and *iso*-BPMEN with dioxygen.

Mechanistic studies

To establish the role of oxygen and water in the decarboxylation reaction of benzilate on **1** and C-N bond cleavage reaction on **2**, reactions were performed with $^{18}O_2$ in the presence or absence of $H_2{}^{18}O$. The result of labelling experiment with **1** and $^{18}O_2$ confirms no incorporation of labeled oxygen into benzophenone. However, the ESI-mass spectrum of the oxidised solution of **2** after the reaction with $^{18}O_2$ shows ion peaks at *m/z* 381.05 and 383.05, supporting the incorporation of two ^{18}O into $[(DPA\text{-}H)Co(picolinate)]^+$ (Figs. 7a and 7c). In addition, the presence of ion peaks at *m/z* 513.05, 515.02, 517.02 and 519.02 support the incorporation of up to four ^{18}O atom into $[Co(BPCA)_2]^+$ (Fig. 7c, Scheme 2). Furthermore, a mixed labelling experiment with **2** and $^{16}O_2$ in the presence of H_2O^{18} demonstrates the incorporation of ^{18}O from H_2O^{18} into $[(DPA\text{-}H)Co(picolinate)]^+$ and $[Co(BPCA)_2]^+$ (Fig. S13) highlighting the involvement of water in the C-N bond cleavage pathway.

Aerial oxidation of the $-CH_2-$ group of *N*-(2-picolyl)picolinamide on cobalt(III) and iron(III) centre has been reported to generate $[M^{III}(BPCA)_2](ClO_4)$ (where M = Co and Fe) complexes.[50] Formation of BPCA from TPA via the dissociation of one of the 2-pyridylmethyl arm and the oxidation at the methyl carbons possibly by atmospheric oxygen on a rhenium complex has been documented.[52] A cobalt(II) complex $[Co(II)(mebpena)]^+$ (mebpena = N-methyl-N,N′-bis(2-pyridylmethyl)ethylene diamine-N′-acetate) of a monoanionic N_4O ligand bearing a pendant carboxymethyl group has been reported to react with O_2 to oxidatively cleave one pyridylmethyl arm of the ligand.[35] [35] In the latter, a cobalt(III)-superoxide species has been proposed to initiate the C-N bond cleavage reaction via abstraction of an H atom from a methylene carbon atom of the ligand. Reactivity studies on a series of cobalt(II) complexes stressed the importance of a coordinatively unsaturated complex for oxidative ligand dissociation by cobalt.[35] [35] The observed reactivity of the complexes reported here is attributed to the presence of vacant coordination site for reaction with O_2. For the cobalt(II)-benzoate complexes, oxygen activation may take place at the metal(II) centre to affect ligand oxidation via H-atom abstraction pathway by a cobalt(III)-superoxide.[53-56] The role of carboxylate co-ligand in the oxidative cleavage of the supporting ligand indicates a dimeric pathway in which the carboxylate may bridge between the two cobalt centre. Involvement of cobalt-oxo type active oxidant, generated via peroxo-bridged dicobalt (III) species, in the oxidative degradation of the ligand is more likely. The incorporation of oxygen atom from labeled water indicates the involvement of cobalt-oxo species in the oxygenation of ligand backbone. However, further investigation is necessary to unravel the exact nature of the active oxidant and the mechanism of the C-N bond cleavage pathway.

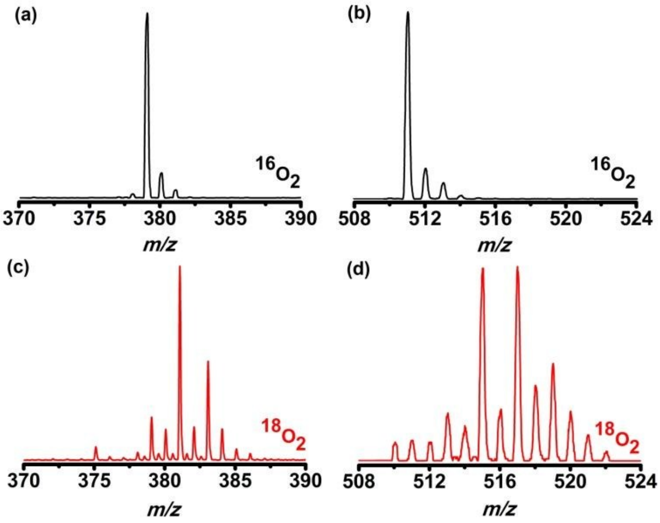


Fig. 7 ESI-mass spectra of the oxidised solution after reaction of **2** with $^{16}O_2$ (a and b) and with $^{18}O_2$ (c and d).

Experimental

Methods and equipment

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All reagents and solvents were purchased from commercial sources and were used without further purification, unless otherwise noted. Solvents were purified and dried prior to use. Acetonitrile was dried over calcium hydride. Triethylamine was dried over sodium prior to use. Preparation and handling of air-sensitive materials were carried out under an inert atmosphere by using standard Schlenk techniques or in a glove box. *Although no problem was encountered during the synthesis of these complexes from $Co(ClO_4)_2$, perchlorate salts are potentially explosive and should be handled with care!*[57] The ligands[12] and the five-coordinate cobalt(II) complexes $[(TPA)Co^{II}(Cl)](ClO_4)$,[43] $[(TPA)Co^{II}(CH_3CN)](ClO_4)$[46] and $[(TPA)Co^{II}(OAc)](BPh_4)$[51] $[(TPA)Co^{II}(benzoylformate)](BPh_4)$[41] were synthesized according to the procedure reported in literature.

Fourier transform infrared spectroscopy on KBr pellets was performed on a Shimadzu FT-IR 8400S instrument. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer. Electron-spray ionization mass spectra were recorded with a Waters QTOF Micro YA263. ^1H NMR spectra were measured at room temperature on Bruker DPX-300 or 500 MHz spectrometer. Solution electronic spectra were measured on an Agilent 8453 diode array spectrophotometer. Room temperature magnetic data were collected on a Gouy balance (Sherwood Scientific, Cambridge, UK). Diamagnetic contributions were estimated for each compound by using Pascal's constants. GC-MS measurements were carried out with a Perkin Elmer Clarus 600 using Elite 5 MS (30 m x 0.25 mm x 0.25 μm) column with a maximum temperature of 300°C. Labelling experiments were carried out with $^{18}O_2$ gas (99 atom %) or H_2O^{18} (98 atom %) purchased from Icon Services Inc., USA.

Syntheses of cobalt(II) complexes. A solution of cobalt(II) perchlorate hexahydrate (0.37 g, 1 mmol) in 5 mL methanol was added to a solution of ligand (1 mmol) in 5 mL methanol. The orange solution was allowed to stir for a while and an equimolar amount of carboxylic acid (benzilic acid or benzoic acid) and Et_3N (140 μL, 1 mmol) in 5 mL methanol was added dropwise. The reaction mixture was further stirred for 4 h. The perchlorate salts were isolated upon addition of diethyl ether to a concentrated reaction solution. Addition of one equivalent of $NaBPh_4$ led to the isolation of tetraphenylborate salts of the complexes.

$[(TPA)Co^{II}(benzilate)](ClO_4)$ (1). Green single crystals were obtained by diffusion of diethyl ether into a THF-CH_3OH (1:1) solution of the complex. Yield: 0.34 g (51%). Elemental analysis calcd (%) for $C_{32}H_{29}ClCoN_4O_7$ (675.98 g/mol): C, 56.86; H, 4.32; N, 8.29. Found: C, 56.72; H, 4.35; N, 8.19. IR (KBr, cm^{-1}): 3429(m), 2924(m), 1609(s), 1485(m), 1443(m), 1377(m), 1115(s), 1092(s), 762(m), 706(m), 623(m). ESI-MS (in positive ion mode, CH_3CN): *m/z* 575.38 (100%, $[(TPA)Co(benzilate)]^+$). UV-vis in CH_3CN (λ_{max}): 467 nm (ε = 150 $M^{-1}cm^{-1}$), 605 nm (ε = 110 $M^{-1}cm^{-1}$), 626 nm (ε = 90 $M^{-1}cm^{-1}$). Magnetic moment μ_{eff} (298 K): 4.29 μ_B. ^1H NMR in CD_3CN (500 MHz, 298 K): δ (ppm) 147.0 (3H, PyH_α), 99.6 (6H, CH_2Py), 52.3 (3H, PyH_β), 45.2 (3H, $PyH_{\beta'}$), 15.6 (1H, benzilate-OH), 9.1 (4H, benzilate-*o*-H), 8.2 (4H, benzilate-*m*-H), 7.4 (2H, benzilate-*p*-H) and -1.2 (3H, PyH_γ).

$[(TPA)Co^{II}(benzoate)](BPh_4)$ (2). Single crystals were obtained by diffusion of diethyl ether into a THF-CH_3OH (1:1) solution of the complex. Yield: 0.55 g (70%). Elemental analysis calcd (%) for $C_{49}H_{43}BCoN_4O_2$ (789.63 g/mol): C, 74.53; H, 5.49; N, 7.10. Found: C, 74.25; H, 5.41; N, 6.98. IR (KBr, cm^{-1}): 3053(m), 1610 (s), 1570(m), 1481(m), 1437(m), 1366(s), 1267(w), 1026(w), 766(m), 733(s), 708(s). ESI-MS (in positive ion mode, CH_3CN): *m/z* 470.10 (100%, $[(TPA)Co(benzoate)]^+$). UV-vis in CH_3CN (λ_{max}): 461 nm (ε = 170 $M^{-1}cm^{-1}$), 607 nm (ε = 115 $M^{-1}cm^{-1}$) and 624 nm (ε = 110 $M^{-1}cm^{-1}$). Magnetic moment μ_{eff} (298 K): 4.32 μ_B. ^1H NMR in CD_3CN (500 MHz, 298 K); δ (ppm) 143.5 (3H, PyH_α), 96.8 (6H, CH_2Py), 49.8 (3H, PyH_β), 45.1 (3H, $PyH_{\beta'}$), 21.6 (2H, benzoate-*o*-H), 14.1 (2H, benzoate-*m*-H), 10.3 (1H, benzoate-*p*-H), 7.3 (8H, BPh_4-Ar-*o*-H), 6.9 (8H, BPh_4-Ar-*m*-H), and 6.7 (4H, BPh_4-Ar-*p*-H) and -0.2 (3H, PyH_γ).

$[($*iso*-BPMEN$)Co^{II}(benzoate)](BPh_4)$ (3). Green solid. Yield: 0.51 g (67%). Elemental analysis calcd (%) for $C_{47}H_{47}BCoN_4O_2$ (769.65 g/mol): C, 73.35; H, 6.16; N, 7.28. Found: C, 72.79; H, 6.12; N, 7.23. IR (KBr, cm^{-1}): 3053(m), 2984(m), 2924(m), 1607(s), 1564(m), 1481(m), 1441(m), 1377(s), 1362(s), 1026(m), 843(m), 758(s), 735(s), 708(s). ESI-MS (in positive ion mode, CH_3CN): *m/z* 450.25 (100%, $[($*iso*-BPMEN$)Co(benzoate)]^+$). UV-vis in CH_3CN (λ_{max}): 468 nm (ε = 160 M^{-1} cm^{-1}), 602 nm (ε = 120 M^{-1} cm^{-1}). Magnetic moment μ_{eff} (298 K): 4.06 μ_B. ^1H NMR in CD_3CN (500 MHz, 298 K); δ (ppm) 153.8 (2H, PyH_α), 126.9 (4H, CH_2Py), 113.9 (3H, N-CH_3), 105.0 (3H, N-CH_3), 71.1 (2H, CH_2), 59.6 (2H, CH_2), 52.4 (2H, PyH_β), 47.0 (2H, $PyH_{\beta'}$), 24.5 (2H, benzoate-*o*-H), 15.0 (2H, benzoate-*m*-H), 11.8 (1H, benzoate-*p*-H), 7.3 (8H, BPh_4-Ar-*o*-H), 7.0 (8H, BPh_4-Ar-*m*-H) and 6.8 (4H, BPh_4-Ar-*p*-H).

Isolation of cobalt(III) complexes. Pure oxygen gas was bubbled through an acetonitrile solution of cobalt (II) complex (**1-3**, $[(TPA)Co^{II}(Cl)](ClO_4)$, $[(TPA)Co^{II}(CH_3CN)](ClO_4)$, $[(TPA)Co^{II}(OAc)](BPh_4)$ and $[(TPA)Co^{II}(benzoylformate)](BPh_4)$) for 5 min and was kept for stirring at room temperature. The resulting green solution slowly turned orange-red over a period of 3-5 d except for $[(TPA)Co^{II}(Cl)](ClO_4)$. The oxidised solution was allowed to stand for few days until crystalline compound separated out from the solution.

$[(DPA)Co^{III}(picolinate)(benzoate)](ClO_4)$ (4). Pure oxygen gas was bubbled through an acetonitrile solution of $[(TPA)Co^{II}(benzoate)](ClO_4)$ (57 mg, 0.10 mmol) for 5 min and was kept for stirring at room temperature. The resulting green solution slowly turned orange-red over a period of 3 d. Single crystals suitable for X-ray diffraction were obtained from a concentrated oxidised solution after 2 weeks. Yield: 19 mg (32%). Elemental analysis calcd (%) for $C_{25}H_{22}ClCoN_4O_8$ (600.85 g/mol): C, 49.97; H, 3.69; N, 9.32. Found: C, 49.93; H, 3.73; N, 9.17. IR (KBr, cm^{-1}): 3439(br), 3706(m), 2926(m), 1724(s), 1670(s), 1607(s), 1572(m), 1475(m), 1448(m), 1337(s), 1284(m), 1090(vs), 625(s). ESI-MS (in positive ion mode, CH_3CN): *m/z* 256.01 (100%, $[(DPA\text{-}2H)Co]^+$), 379.05 (80%, $[(DPA\text{-}H)Co(picolinate)]^+$), 501.00 (10%, $[(DPA)Co(picolinate)(benzoate)]^+$). ^1H NMR (300 MHz, CD_3CN, 298 K): δ (ppm) 12.17 (br, s, 1H), 9.73 (d, 1H, *J* = 4.8 Hz), 8.48

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(m, 2H), 8.13 (d, 1H, J = 7.2 Hz), 7.98 (t, 2H, J = 7.5 Hz),7.81 (d, 2H, J = 7.5 Hz), 7.61 (t, 4H, J = 7.0 Hz), 7.45 (t, 1H, J = 7.2 Hz), 7.33 (m, 4H), 5.06 (m, 2H), 4.87 (m, 2H).

$[(BPCA)_2Co^{III}](BPh_4)$ (5). Red crystals suitable for X-ray diffraction were isolated from a concentrated solution of the oxidised species of **2** (78 mg, 0.10 mmol) after 3 weeks. Yield: 16 mg (38%). Elemental analysis calcd (%) for $C_{48}H_{36}BCoN_6O_4$ (830.58 g/mol): C, 69.41; H, 4.37; N, 10.12. Found: C, 68.95; H, 4.26; N, 10.11%. IR (KBr, cm^{-1}): 3526(br), 3445(br), 3049(m), 2928(m), 1720(s), 1651(m), 1606(m), 1337(s), 1296(m), 762(m), 736(m), 700(s). ESI-MS (in positive ion mode, CH_3CN): m/z 511.02 (100%, $[(BPCA)_2Co]^+$). ^1H NMR (300 MHz, CD_3CN, 298 K): δ (ppm) 8.35 (d, 4H, J = 5.3 Hz), 8.21 (d, 4H, J = 7.3Hz), 8.09 (t, 4H, J = 7.7 Hz), 7.5 (t, 4H, J = 7.1 Hz), 7.3 (m, 8H), 7.0 (t, 8H, J = 7.4 Hz), 6.8 (t, 4H, J = 7.2 Hz).

$[(DPEA)Co^{III}$(picolinate)(benzoate)](BPh_4) (6). After two weeks, addition of diethyl ether to the oxidised solution of **3** (77 mg, 0.10 mmol) results in the isolation of a red solid. Yield: 49 mg (62%). Elemental analysis calcd (%) for $C_{47}H_{46}BCoN_4O_4$ (800.64 g/mol): C, 70.51; H, 5.79; N, 7.00. Found: C, 69.95; H, 5.66; N, 7.11%. IR (KBr, cm^{-1}): 3462(br), 3049(m), 2926(m), 1670(s), 1603(s), 1475(m), 1387(s), 1348(m), 733(s), 708(s). ESI-MS (in positive ion mode, CH_3CN): m/z 236.01 (100%, [(DPEA-2H)Co]$^+$), 359.09 (90%, [(DPEA-H)Co(picolinate)]$^+$), 481.13 (30%, [(DPEA)Co(picolinate)(benzoate)]$^+$). ^1H NMR (300 MHz, CD_3CN, 298 K): δ (ppm) 12.22 (br, s, 1H), 9.54 (d, 1H, J = 4.8 Hz), 8.44 (t, 1H, J = 5.0 Hz), 8.28 (t, 1H, J = 7.2 Hz), 8.11 (d, 1H, J = 5.0 Hz), 7.89 (d, 3H, J = 9.0 Hz), 7.51 (m, 3H, J = 7.0 Hz), 7.39 (m, 2H, J = 7.2 Hz), 7.21 (m, 8H), 7.11 (t, 1H, J = 7.4 Hz), 6.94 (t, 8H, J = 7.5 Hz), 6.81 (t, 4H, J = 7.3 Hz), 4.88 (m, 2H), 4.48 (m, 2H), 3.37 (m, 2H), 3.28 (m, 3H), 3.20 (m, 3H).

$[\{(TPA)Co^{III}(OH)\}_2](ClO_4)_4$ (7). Dry oxygen gas was purged through the solution $[(TPA)Co^{II}(CH_3CN)](ClO_4)_2$ (63 mg, 0.10 mmol) in acetonitrile (10 mL) for 5 min and was kept under oxygen atmosphere. The pink solution slowly turned red over a week. Single crystals suitable for X-ray diffraction were isolated from the acetonitrile solution upon addition of 5 mL methanol to the oxidised solution in diethyl ether. Yield: 47 mg (82%). Elemental analysis calcd (%) for $C_{36}H_{38}Cl_4Co_2N_8O_{18}\cdot CH_3CN$ (1171.46 g/mol): C, 38.96; H, 3.53; N, 10.76. Found: C, 38.58; H, 3.60; N, 10.51. IR (KBr, cm^{-1}): 3408(br), 3049(m), 2933(m), 1609(s), 1481(m), 1445(m), 1288(m), 1144, 1115, 1086(s), 775(m), 627(s).

Reaction of cobalt(II)-benzilate complex, 1 with oxygen and analysis of organic products. Solid complex (0.10 mmol) was dissolved in dry acetonitrile (15 mL) under nitrogen atmosphere. Pure oxygen gas was bubbled through the solution and was allowed to stir at room temperature for 4 h, during which the initial light yellow solution slowly turned light orange. The solution was concentrated and to the residue was added 10 mL 2*M* HCl. The organic products were then extracted with diethyl ether (3 × 20 mL), dried over sodium sulphate and evaporated under reduced pressure. The products were analysed and quantified by GC-MS and ^1H NMR spectroscopy with respect to internal standard. Quantification of benzophenone (from benzilate complexes) was performed by comparing the peak area of four aromatic *ortho*-protons of benzophenone (δ 7.81 ppm) with respect to the aromatic protons of 2,4-di-*tert*-butylphenol at δ 6.63 ppm in $CDCl_3$. Benzophenone: ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, 4H), 7.60 (t, 2H), 7.51 (t, 4H).

X-ray crystallographic data collection and refinement of the structures. Crystallographic data for complexes **1**, **2**, **4**$\cdot CH_3CN$, **5** and **7**$\cdot 2CH_3CN$ are provided in Tables S1 and S3. Diffraction data were collected at 120 K for all the complexes on a Bruker Smart APEX II (Mo-K_α radiation, λ = 0.71073 Å). Cell refinement, indexing and scaling of the data set were carried out using the APEX2 v2.1-0 software.[58] The structures were solved by direct methods and subsequent Fourier analyses and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[59] In all the complexes hydrogen atoms are fixed and all the non-hydrogen atoms are refined anisotropically. One of the oxygen atoms (O8) of the perchlorate anion in **4**$\cdot CH_3CN$ was found disordered and fixed over three position. In complex **7**$\cdot 2CH_3CN$, hydrogen atom of the hydroxide coordinated to the cobalt(II) centre could not be located. CCDC 1964010, 1964012, 1964011, 1964013 and 1964014 contain the supplementary crystallographic data for **1**, **2**, **4**, **5** and **7**$\cdot 2CH_3CN$, respectively. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

DFT Calculations. Density functional theory (DFT) calculations of the complexes were carried out using the Gaussian 09 program package.[60] The five-coordinate geometry of **1** and **2** were optimised with the cartesian coordinates obtained from the crystal structures of the complexes whereas those of complex **3** were obtained from the previously reported complex [*iso*-BPMEN)Co^{II}(salicylate)]$^+$.[42] GaussView5 software package was used for generating input file and for analysis of bond distances and angles around metal centre and different spin density plot. The local minima with positive eigenvalues were ensured for performing the vibrational frequency calculations with the optimised geometries. The energies reported for the optimised geometries included zero-point and free energy corrections.

Conclusions

Three five-coordinate cobalt(II) complexes of tripodal N4 ligands with benzilate or benzoate co-ligand were isolated and characterised. The cobalt(II)-benzoate complexes activate dioxygen to carry out oxidative ligand dissociation via C-N bond cleavage of one of the pyridylmethyl arms. The cobalt(II)-benzilate complex of the TPA ligand, which does not exhibit ligand oxidation, undergoes decarboxylation of the coordinated benzilate in the reaction with dioxygen. Labelling experiments with $^{18}O_2$ and $H_2{}^{18}O$ confirm the involvement of dioxygen and water in ligand cleavage pathway. The results described herein show the importance of carboxylate co-ligands in the dioxygen activation at the coordinatively unsaturated cobalt(II) centre and on the oxidative C-N bond cleavage of the supporting ligand by a cobalt-oxygen oxidant. This study reveals that cobalt-carboxylate complexes of (2-pyridylmethyl)amine-based ligands are not stable under

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oxidising conditions and therefore these ligands may not be suitable candidates for homogeneous oxidation catalysis. Further investigations to unravel the exact nature of the active oxidant responsible for the ligand oxidation are being carried out in our laboratory.

Conflicts of interest

Authors declare no conflicts of interest.

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