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Trapping of superoxido cobalt and peroxido dicobalt species formed reversibly from Co^{II} and $\text{O}_2^\dagger$

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The formation and spectroscopic characterization of a superoxido cobalt(III) and a peroxido dicobalt(III) species formed in the temperature dependent reversible reaction of a cobalt(II) precursor with O_2 is described. The electronic nature of each species is explored in their reactivity with organic substrates.

Oxygen activation by first-row transition metal complexes is a vital field of inquiry, not least in the detection and characterization of a wide range of mono- and multi-metallic compounds ligated by activated forms of O_2 (including superoxide, peroxide and oxide).^{1–8} The biological relevance of copper and iron has stimulated such studies for these two metals and the development of bioinspired models of selected O_2 -activating enzymes.

Cobalt–dioxygen adducts, although of less biological relevance, are of interest,⁹ in large part due to the thermodynamic and kinetic stability of their low spin Co^{III} complexes. Such compounds were widely studied in the 1970s and 1980s^{10–12} and in these early biomimetic investigations, the relative stability of Co^{III} –dioxygen complexes provided information on the structure and physico-chemical properties of transition metal– O_2 adducts. For instance, coboglobin, an analogue of hemoglobin in which cobalt replaces iron, was used to structurally mimic the O_2 transporter.¹³ Several Co–O_2 adducts are particularly interesting as intermediates in

cobalt-catalysed oxidation reactions. Peroxido cobalt species are nucleophilic oxidants^{14–17} whereas peroxido dicobalt compounds are potential intermediates in the 4e^- oxidation of water^{18,19} and in the reverse reduction of molecular O_2 to water.^{20,21}

Herein, we report the reversible activation of O_2 by the mononuclear cobalt(II) complex $[\text{Co}^{\text{II}}(\text{Pytaen})(\text{CH}_3\text{CN})_2]^{2+}$ (**1**, Scheme 1)²² with initial formation of a mononuclear superoxido cobalt(III) species (**2**) followed by stabilisation and formal double reduction of O_2 through the formation of a peroxido bridged dicobalt(III) complex (**3**). The reactivity of both species towards organic substrates is explored. The trapping and characterisation of both species at low temperatures by UV-vis absorption, ^1H NMR and resonance Raman (rR) spectroscopies is described and their chemistry compared with that of earlier described metal–dioxygen systems.

UV-vis absorption spectroscopy indicates that **1** does not react with O_2 at $+25^\circ\text{C}$ in acetonitrile. At -35°C , however, the UV-vis absorption spectrum of **1** changes with the appearance of two intense bands at 395 nm ($\epsilon = 4500\text{ M}^{-1}\text{ cm}^{-1}$) and 505 nm ($\epsilon = 2900\text{ M}^{-1}\text{ cm}^{-1}$) over ~ 20 min, corresponding to a new species (**3**), which is stable for >4 h (Fig. 1a). The original spectrum of **1** was recovered by purging the solution of **3** with N_2 gas at -35°C (Fig. S15, ESI†) or by increasing the temperature to $+25^\circ\text{C}$. Similar temperature-dependent reversible binding of O_2 has been demonstrated for Co^{II} complexes earlier.^{21,23}

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Scheme 1 The reversible reaction of $[\text{Co}^{\text{II}}(\text{Pytaen})(\text{CH}_3\text{CN})_2]^{2+}$ (**1**) with O_2 .

Fig. 1 (a) UV-vis absorption spectra of the reaction of **1** (0.4 mM black line) in MeCN with O₂ at –35 °C to form compound **3** (red line). Inset: Time trace of the band at 505 nm. (b) ¹H NMR spectra of **1** in CD₃CN in the presence of O₂ at +25 °C (black) and –35 °C (red, with expansion of 10–0 ppm region shown below).

The reversibility of the reaction between **1** and O₂ was established by variable temperature ¹H NMR spectroscopy. **1**, which is a high spin cobalt(II) complex ($\mu_{\text{eff}} = 4.73 \mu_{\text{B}}$ at +25 °C),²⁴ exhibits paramagnetically shifted ¹H NMR signals (Fig. S1, ESI†), which are unaffected at room temperature by the presence of O₂ (Fig. 1b). However, they decrease in intensity in the presence of O₂ at –35 °C with new signals in the diamagnetic region appearing, corresponding to the low spin cobalt(III) compound **3**. Two sets of pyridine signals with similar chemical shifts were observed in a 2 : 3 ratio, as confirmed by 2D ¹H NMR spectroscopy (Fig. S7 and S8, ESI†). The spectrum of **1** fully recovers upon warming to room temperature. One electron oxidation of **1** to give the corresponding cobalt(III) complex can be excluded, since the ¹H NMR spectrum of [Co^{III}(Pytacn)(CH₃CN)₂](SbF₆)₃ (**1**⁺SbF₆), prepared independently, is distinct from that **3** (Fig. S3, ESI†).

The Raman spectrum (λ_{exc} 532 nm) of frozen (77 K) solutions of **3** in MeCN show enhancement of bands at 804 and 825 cm^{–1} that are typical of peroxido dicobalt(III) O–O stretching modes.^{18,25–27} These bands shift to 761 and 778 cm^{–1} with ¹⁸O₂, respectively (calcd shift for $\nu_{\text{O-O}}$ mode $\Delta[\text{^{18}\text{O}] = -47 \text{ cm}^{-1}}$, Fig. 2). The observation of

Fig. 2 Resonance Raman spectra (at 77 K) of **3** (1.2 mM) in MeCN (λ_{exc} 532 nm) formed by reaction of **1** with ¹⁶O₂ (blue line) and with ¹⁸O₂ (green line). Red line corresponds to the spectrum with ¹⁸O₂ after scaled subtraction of the spectrum with ¹⁶O₂. Black line corresponds to a spectrum of MeCN alone.

two distinct $\nu_{\text{O-O}}$ bands is consistent with the two sets of pyridine signals in the ¹H NMR spectrum of **3** (*vide supra*). A less intense band at 569 cm^{–1}, tentatively assigned to a Co–O mode, is also isotope sensitive ($\Delta[\text{^{18}\text{O}] = -18 \text{ cm}^{-1}}$) with a shift close to that expected for a Co–O bond ($\Delta[\text{^{18}\text{O}] = -25 \text{ cm}^{-1}}$). These bands disappear upon warming to room temperature and reappear as the temperature is decreased again. Overall the data indicate that **3** is a peroxido dicobalt(III) species formed by the reversible reaction of two molecules of **1** with O₂.

Notably, addition of O₂ to **1** at –80 °C in acetone results in the formation of another species (**2**) within 1 min, with two absorption bands at 375 nm ($\epsilon = 6350 \text{ M}^{-1} \text{ cm}^{-1}$) and 520 nm (Fig. S9, ESI†). The ¹H NMR spectrum of **2** in d₆-acetone at –80 °C shows paramagnetically shifted signals over a 340 ppm range, consistent with a paramagnetic superoxido cobalt(III) species (Fig. S10, ESI†). The CW X-band EPR spectrum of **2** recorded in acetone at 100 K displays an axial $S = 1/2$ signal that can be assigned to a Co^{III}-superoxo species based on the comparison of the corresponding EPR parameters ($A_{\parallel} = 1.59 \text{ mT}$ due to ⁵⁹Co ($I = 7/2$) nucleus, $g_{\parallel} = 2.0808$, $g_{\perp} = 1.99$) and those reported in the literature for previously described superoxido cobalt(III) complexes⁹ (Fig. S11, ESI†). Unfortunately, Raman spectroscopy at λ_{exc} 355 nm and at λ_{exc} 523 nm do not show resonance enhancement of any vibrational bands. **2** is indefinitely stable at –80 °C but converts to the peroxide bridged dicobalt(III) species (**3**) when the temperature is increased. Thus, when a solution of **2** at –80 °C was warmed up to –35 °C the visible absorption and rR bands of **3** appeared (Fig. S12 and S13, ESI†) and the paramagnetic ¹H NMR spectrum of **2** converted into the diamagnetic NMR spectrum of **3** (Fig. S10, ESI†). Importantly, the spectroscopic features of **2** were not recovered when the temperature was lowered again, indicating that the conversion of **3** to **2** is thermodynamically downhill and that **2** is a kinetic product (Fig. S12, ESI†). However, **2** can be converted directly back to **1** at –80 °C when the solution was purged with N₂ (Fig. S14, ESI†). Notably the absorption band at 520 nm was essentially unaffected by N₂ purging, indicating that it originates from a small amount of **3** formed at –80 °C also.

Further support for the structures assigned to **2** and **3** and the mechanism for their formation was provided by DFT methods (B3LYP functional with the TZVP basis set for all

Fig. 3 Lowest free energy profile for the reaction of **1** with O₂ in MeCN at 238.15 K to form **2**. Gibbs energies are given in kcal mol^{−1}.

atoms including solvent and dispersion effects. See ESI† for more details). The mononuclear superoxido cobalt(III) species (**2**) was considered to form by substitution of an acetonitrile ligand of **1** by O₂ ($\Delta G = +2.3$ kcal mol^{−1} at −35 °C) concomitant with inner sphere electron transfer between cobalt(II) and O₂ (Fig. 3). Formation of [Co^{III}(O₂)(Pytacn)(CH₃CN)]²⁺ (**2**) has a free energy cost of +3.7 kcal mol^{−1} and the process is kinetically feasible under reaction conditions ($\Delta G^\ddagger = +6.5$ kcal mol^{−1}). In the optimized structure, the superoxide moiety in **2** is bound in a η^1 end-on fashion to the metal center *trans* to one of the N-Me units of the Pytacn ligand. The O₂-adduct preceding the formation of the alternative isomer with the superoxido unit *trans* to the NCH₂Py group was significantly less favored (adduct b, $\Delta G = +5.1$ kcal mol^{−1}, Fig. 3). Mulliken spin density analysis revealed that almost no spin density is present on the cobalt center in **2** ($\rho(\text{Co}) = -0.10$) and one unpaired electron is delocalized on the dioxygen moiety ($\rho(\text{O}_2) = 1.10$), confirming the superoxide character of the bound O₂ unit (Fig. S21, ESI†). Furthermore, the calculated Co-O and O-O bond distances (1.92 Å and 1.29 Å, respectively) are consistent with a superoxido metal species.²⁸ Formation of a superoxido cobalt(III) species with a η^2 side-on O₂ moiety (involving the loss of the two acetonitrile ligands from **1**) is energetically inaccessible ($\Delta G^\ddagger = +26.6$ kcal mol^{−1}, Fig. S22, ESI†).

Compound **2** is not detected at −35 °C and when formed at −80 °C followed by heating it forms the peroxido dicobalt(III) compound (**3**). Optimization of the structure of **3** indicates that the O₂ moiety binds in a μ - η^1 : η^1 *trans* configuration (*cis*- μ - η^1 : η^1 or side-on μ - η^2 : η^2 binding modes were also considered but they evolved to *trans*- μ - η^1 : η^1). Several isomers of **3** (*S* = 0) are possible, which arise from the relative orientation between the pyridines of the two Pytacn ligands, and the disposition of the oxygen atoms of the peroxido unit within the coordination sphere of

each cobalt center (*trans* to a NMe or to the NCH₂Py group of the Pytacn ligand, see Fig. S23, ESI†). Taking into account that the oxygen atom in **2** binds *trans* to a NMe group, in **3** coordination of the oxygen atoms must occur in this position. Thus, isomers **3a** and **3b** (Fig. 4), which have approximately C₂ symmetry and differ only in the relative disposition of the pyridine rings of the two Pytacn ligands (with N_{py}-Co-Co-N_{py} torsion angles of 72° and 161°, respectively) are the most feasible structures for **3**. These two isomers may correspond to the two species observed in the ¹H NMR and rR spectra of **3**. The relative energies of the O-O vibrations measured at 825 and 804 cm^{−1}, and the corresponding shift with ¹⁸O₂ (−47 and −43), agree well with those calculated for **3a** and **3b**, respectively (scaled vibration frequencies of 908 and 891 cm^{−1}, that shift to 859 and 841 cm^{−1} upon ¹⁸O labeling, Fig. S25, ESI†). Interestingly, the formation of **3a** and **3b** is thermodynamically downhill at −35 °C (−0.6 and −4.9 kcal mol^{−1}, respectively), but it becomes progressively less favored upon increasing the temperature (Fig. S24, ESI†). This occurs because the oxygenation of **1** is an exothermic process ($\Delta H < 0$) with a negative entropy change ($\Delta S < 0$) that only occurs at low temperatures when ΔH dominates over the $-T\Delta S$ factor, which explains the lack of reactivity of **1** with O₂ at higher temperatures.

The reactivity of **2** and **3** with organic substrates supports their assignments. **3** does not react with O-H or C-H bonds in 2,4,6-tri-*tert*-butylphenol and 9,10-dihydroanthracene, respectively, and does not oxidize olefins (*e.g.* cyclooctene) or sulfides (*e.g.* thioanisole). Instead, **3** reacts with aldehydes, manifested in the exponential decrease in its UV-vis absorbance upon addition of excess cyclohexane carboxaldehyde or 2-phenylpropionaldehyde. Observed rate constants (*k*_{obs}) are linearly dependent on the concentration of substrate with second order rate constants of 0.021 M^{−1} s^{−1} and 0.0011 M^{−1} s^{−1}, respectively (Fig. S19, ESI†). Reaction of **3** with a series of *para*-substituted benzaldehydes (*para*-X-PhCHO, X = OMe, Me, F, H, Cl) affords a Hammett ρ value of +1.8 (Fig. S20, ESI†) consistent with a nucleophilic species. These data further support the assignment of **3** as a peroxido metal species, which typically behave as nucleophiles.^{14–17}

In contrast, **2** only engages in hydrogen atom transfer (HAT) from O-H bonds; *i.e.* addition of excess 2,4,6-tri-*tert*-butylphenol to **2** in acetone at −80 °C results in a decrease in the absorbance at 375 nm, concomitant with an increase in the deep blue colour of the 2,4,6-tri-*tert*-butylphenoxyl radical (Fig. S16, ESI†), with a second order rate constant of 0.59 M^{−1} s^{−1} and a KIE of 2.4 (*d*₁-TTBP, Fig. S17, ESI†). These data indicate that the rate

Fig. 4 DFT computed structure for peroxido dicobalt(III) compounds **3a** and **3b** (other possible isomers of **3** are depicted in Fig. S23, ESI†).

determining step involves cleavage of the O–H bond.^{29,30} Indeed, several superoxido metal complexes are reactive towards phenols,^{29,31,32} which supports the assignment of **2** as a superoxido cobalt compound.

In the present contribution we show that the cobalt(II) complex **1** reacts reversibly with O₂ to form, initially, a superoxido cobalt(III) species (**2**) that can be trapped at –80 °C and subsequently a peroxido dicobalt(III) complex (**3**), observed at –35 °C. The data indicate that the formation of mononuclear and subsequently dinuclear complexes is a stepwise and reversible process. Despite that cobalt–dioxygen chemistry has been studied extensively and kinetic studies of O₂ uptake by cobalt(II) complexes indicate that the formation of peroxido dicobalt(III) complexes is always preceded by the formation of the corresponding superoxido cobalt(III),^{33,34} to the best of our knowledge the work reported here constitutes the first example of the direct detection of a relatively stable superoxido precursor prior to the generation of the corresponding peroxido dimer. This observation further supports the idea that this mechanism, widely accepted in copper–dioxygen chemistry, applies also to cobalt.

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Conflicts of interest

There are no conflicts to declare.

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