Catalytic dioxygen reduction mediated by a tetranuclear cobalt complex supported on a stannoxane core†

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The synthesis, spectroscopic characterization (infrared, electron paramagnetic resonance and X-ray absorption spectroscopies) and density functional theoretical calculations of a tetranuclear cobalt complex \( \text{Co}_4\text{L}_1 \) involving a nonheme ligand system, \( \text{L}_1 \) supported on a stannoxane core are reported. \( \text{Co}_4\text{L}_1 \), similar to the previously reported hexanuclear cobalt complex \( \text{Co}_6\text{L}_2 \), shows a unique ability to catalyze dioxygen (\( \text{O}_2 \)) reduction, where product selectivity can be changed from a preferential \( 4\text{e}^-/4\text{H}^+ \) dioxygen-reduction (to water) to a \( 2\text{e}^-/2\text{H}^+ \) process (to hydrogen peroxide) only by increasing the temperature from \(-50 \) to \( 30 \) °C. Detailed mechanistic insights were obtained on the basis of kinetic studies on the overall catalytic reaction as well as by low-temperature spectroscopic (UV-Vis, resonance Raman and X-ray absorption spectroscopies) trapping of the end-on \( \mu_1,2\)-peroxodicobalt(III) intermediate \( \text{I} \). The \( \text{Co}_4\text{L}_1 \)- and \( \text{Co}_6\text{L}_2 \)-mediated \( \text{O}_2 \)-reduction reactions exhibit different reaction kinetics, and yield different ratios of the \( 2\text{e}^-/2\text{H}^+ \) and \( 4\text{e}^-/4\text{H}^+ \) products at \(-50 \) °C, which can be attributed to the different stabilities of the \( \mu_1,2\)-peroxodicobalt(III) intermediates formed upon dioxygen activation in the two cases. The deep mechanistic insights into the transition-metal mediated dioxygen reduction process that are obtained from the present study should serve as useful and broadly applicable principles for future design of more efficient catalysts in fuel cells.

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Abstract:

The synthesis, spectroscopic characterization (infrared, electron paramagnetic resonance and X-ray absorption spectroscopies) and density functional theoretical calculations of a tetranuclear cobalt complex \( \text{Co}_4\text{L}_1 \) involving a nonheme ligand system, \( \text{L}_1 \) supported on a stannoxane core are reported. \( \text{Co}_4\text{L}_1 \), similar to the previously reported hexanuclear cobalt complex \( \text{Co}_6\text{L}_2 \), shows a unique ability to catalyze dioxygen (\( \text{O}_2 \)) reduction, where product selectivity can be changed from a preferential \( 4\text{e}^-/4\text{H}^+ \) dioxygen-reduction (to water) to a \( 2\text{e}^-/2\text{H}^+ \) process (to hydrogen peroxide) only by increasing the temperature from \(-50 \) to \( 30 \) °C. Detailed mechanistic insights were obtained on the basis of kinetic studies on the overall catalytic reaction as well as by low-temperature spectroscopic (UV-Vis, resonance Raman and X-ray absorption spectroscopies) trapping of the end-on \( \mu_1,2\)-peroxodicobalt(III) intermediate \( \text{I} \). The \( \text{Co}_4\text{L}_1 \)- and \( \text{Co}_6\text{L}_2 \)-mediated \( \text{O}_2 \)-reduction reactions exhibit different reaction kinetics, and yield different ratios of the \( 2\text{e}^-/2\text{H}^+ \) and \( 4\text{e}^-/4\text{H}^+ \) products at \(-50 \) °C, which can be attributed to the different stabilities of the \( \mu_1,2\)-peroxodicobalt(III) intermediates formed upon dioxygen activation in the two cases. The deep mechanistic insights into the transition-metal mediated dioxygen reduction process that are obtained from the present study should serve as useful and broadly applicable principles for future design of more efficient catalysts in fuel cells.

Introduction:

Significant, attention has been focused in recent years on the synthesis of transition metal based dendrimer structures owing to their diverse applications in various fields. In particular, these dendrimers, in many cases, allow synergistic interactions between the individual transition metal centers in carrying out a variety of important transformations. The organonoxotin clusters are in particular attractive because of the diversity of arrangements that they adopt, such as ladder, O-capped, cube, butterfly, drum, one, two and three-dimensional structures, (1D, 2D, and 3D). Furthermore, incorporation of redox-active transition-metal centers into the stannoxane clusters has previously led to the demonstration of important reactivity patterns. For example, an extensive cooperative effect between the Cu centers was observed during the cleavage of supercoiled DNA catalyzed by a hexanuclear Cu-porphyrin complex, supported on a stannoxane core. In our group we have previously demonstrated the ability of a non-heme stannoxane based hexanuclear ligand system to undergo O–O bond formation and O–O bond cleavage reactions, when bound to iron(II) and cobalt(II) centers, respectively. In the present manuscript we report the synthesis, characterization and X-ray structure of a tetranuclear stannoxane based non-heme ligand system \( \text{L}_1 \), and a detailed kinetic study of the catalytic dioxygen reduction reaction mediated by the corresponding cobalt complex \( \text{Co}_4\text{L}_1 \). Notably, catalytic reductions of \( \text{O}_2 \) to water or \( \text{H}_2\text{O}_2 \) have tremendous technological significance. However, in contrast to biology, where cheap and readily available transition-metal complexes of Fe, and Cu are employed for \( \text{O}_2 \) reduction, high loadings of a precious metal like platinum is warranted for achieving appreciable reactivity during abiological \( \text{O}_2 \)-reduction reactions. Thus the present study is relevant to the ongoing research activities that are being dedicated towards the development of \( \text{O}_2 \) reduction catalysts based on nonprecious.
metals. Furthermore, it provides deep mechanistic insights into the factors that control two- vs. four-electron reductions of O₂, thereby providing useful and broadly applicable principles for the future design of more efficient O₂ reduction catalysts.

Results and discussion

Synthesis and characterisation of L₁

The condensation reaction (Schemes S1 and S2†) of equimolar amounts of di-n-butyltin oxide and 4-[1,3-bis(2-pyridylmethyl)-2-imidazolidinyl]benzoic acid in toluene afforded L₁ as a pale yellow solid. The molecular structure of L₁ shows that a planar Sn₄O₂ core supports the four metal-binding sites (Fig. 1: top). This is in contrast to the situation reported earlier for the hexanuclear non-heme ligand system L₂, where six metal-binding sites were located in a wheel-like arrangement around a central Sn₆O₆ prismane core (Fig. 1: bottom). The stannoxane core in Ligand L₁ adopts a ladder framework with two central and two terminal tin atoms. The tetranuclear structure of L₁ is maintained in solution. ¹¹⁹Sn NMR spectrum of L₁ exhibits two sharp singlets of equal intensity at −210.82 ppm and −213.81 ppm (Fig. S1†), which is the characteristic signature for a planar Sn₄O₂ core.²–⁶ The infrared spectrum shows four vibrations at 1622 cm⁻¹, 1591 cm⁻¹, 1569 cm⁻¹, and 1545 cm⁻¹ for the carboxyl absorptions (νCOO), and one strong band at 682 cm⁻¹ assigned to νSn–O for the Sn₄O₂ core (Fig. S2†).

Synthesis and characterization of Co₄L₁

The reaction of L₁ with 4 equiv. of Co(CF₃SO₃)₂ in acetone yields Co₄L₁ as a dark yellow powder in 70% yield (Scheme 1). The C, H, and N content of Co₄L₁, determined by elemental analysis, established the presence of four cobalt atoms per tetrameric ligand, with two triflates associated with each cobalt (see ESI†). The infrared spectrum of Co₄L₁ depicts the characteristic vibrations of the Sn₄O₂ core at 1625 cm⁻¹, 1593 cm⁻¹, 1572 cm⁻¹, 1549 cm⁻¹, and 682 cm⁻¹ (Fig. S2†). These vibrations are only slightly shifted relative to that of L₁, which reveals that the tetranuclear arrangement is also maintained in Co₄L₁.

Electronic and structural information of Co₄L₁ were obtained from X-ray absorption spectroscopy (XAS) in conjunction with density functional theory (DFT) calculations. The near edge structure (XANES) was used for determination of the oxidation states, whereas the extended fine structure (EXAFS) unraveled the local site geometries around the Co atoms. The spectra are displayed in Fig. 2, the corresponding fit values are collected in Table 1. The XANES spectrum of Co₄L₁ (blue trace) is displayed together with spectra from Co reference compounds of known oxidation states (Co²⁺, Co².₆₆⁺, Co³⁺), see Fig. 2a; it is consistent with a Co²⁺ oxidation state in Co₄L₁. 

![Scheme 1](image-url) 

Scheme 1  Synthesis of the tetra-nuclear cobalt(II) complex (Co₄L₁) from the tetra-nuclear stannoxane ligand (L₁) and the formation of the cobalt (II)–peroxo complex (1).
The EXAFS of Co$_4$L$_1$ could be well fitted by four shells, with one shorter N-shell with coordination number ($N$) of 5, a longer N/O-shell with $N = 1$, and two C-shells with $N = 3$ and 2 (Fig. 2c and d). Attempts to fit Co$_4$L$_1$ with a sum of $N = 5$ in the first two shells (instead of 6) significantly worsen the fit parameters. In principle, there are up to nine C-atoms within a radius of 3.5 Å around the Co-atom, however, due to the pronounced inhomogeneity of the Co–C distances, these shells may partially cancel each other out. The average Co–O/N distance is found to be 2.17 Å.

Since there are no X-ray diffraction (XRD) structures available for Co$_4$L$_1$ and the Co atoms are mainly surrounded by O, N and C atoms with similar scattering properties, the EXAFS fits may suffer from non-uniqueness and misinterpretations. In order to reduce this problem as well as to obtain suitable phase functions for the fits, DFT calculations were conducted in the experimentally observed (from EPR; Fig. S3†) $S = 3/2$ spin state for a series of potential structural variants of the monomeric subsection of the organic ligands, starting from the modified XRD structure of the tetrameric stannoxane ligand (see Fig. 3 and S4†). This approach is justified as there are no intra-molecular electronic interactions detectable between adjacent Co(II) sites, as evident from the X-band EPR spectrum of Co$_4$L$_1$, which exhibits a major axial signal with effective $g^\perp = 4.01$ and $g^\parallel \approx 2.0$ corresponding to the $S = 3/2$ ground state (Fig. S3†). Structural variants include the

### Table 1 EXAFS fit parameters for Co$_4$L$_1$ and 1

| Model       | Shell | $N^a$ | $R$ (Å) | Err  | $\sigma$ (Å) | Err  |
|-------------|-------|-------|---------|------|--------------|------|
| Co$_4$L$_1$ | Co–N  | 5     | 2.14    | 0.01 | 0.056        | 0.007|
|             | Co–N  | 1     | 2.34    | 0.05 | 0.056        |      |
|             | Co–C  | 3     | 2.94    | 0.03 | 0.056        |      |
|             | Co–C  | 2     | 3.06    | 0.05 | 0.056        |      |
| 1           | Co–N  | 4     | 1.91    | 0.01 | 0.036        | 0.009|
|             | Co–O  | 1     | 2.02    | 0.03 | 0.036        |      |
|             | Co–C  | 3     | 2.78    | 0.03 | 0.036        |      |
|             | Co–C  | 2     | 2.92    | 0.05 | 0.036        |      |

$a$ Value kept constant in the final refinement. Amplitude reduction factor $S_0^2 = 0.95$. $N$ represents the EXAFS coordination number, $R$ the absorber-backscatter distance and $\sigma$ the Debye Waller parameter.

(Fig. 2b). The EXAFS of Co$_4$L$_1$ could be well fitted by four shells, with one shorter N-shell with coordination number ($N$) of 5, a longer N/O-shell with $N = 1$, and two C-shells with $N = 3$ and 2 (Fig. 2c and d). Attempts to fit Co$_4$L$_1$ with a sum of $N = 5$ in the first two shells (instead of 6) significantly worsen the fit parameters. In principle, there are up to nine C-atoms within a radius of 3.5 Å around the Co-atom, however, due to the pronounced inhomogeneity of the Co–C distances, these shells may partially cancel each other out. The average Co–O/N distance is found to be 2.17 Å.

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coordination of triflate (OTf) and/or solvent acetone molecules in cis- or trans-orientations, and with or without inherent molecular symmetry, (see legend of Fig. S4†). Four of the six DFT models show hexa-coordinated Co[n] (no. 1, 2, 5, and 6), and the other two show penta-coordination (no. 3 and 4; see Table S1†). Since unrestrained EXAFS fits of Co4L1 clearly indicate hexa-coordination, the corresponding DFT models are considered to be closer to the actual structure of Co4L1. The average Co–X (X = N, O) bond distances, however, vary in the narrow range of 2.09 to 2.19 Å in all six models, which can hardly be discriminated by EXAFS, but all of them are close to the 2.17 Å obtained from the experiments.

The lowest molecular energy is obtained for the hexa-coordinated model 5, followed by penta-coordinated model 3, which is only 5 kJ mol\(^{-1}\) higher in energy. Fine structural details are visible in the EXAFS wave, which promises more insight into the real structure than geometric and energetic considerations alone. Accordingly, EXAFS was calculated for all six small DFT models and compared to the experimental spectra of Co4L1, as seen in Fig. S5 in the ESI.† Here again, model 5 apparently gives the best match to the spectrum of Co4L1, followed by the other hexa-coordinate models 2, 6 and 1, whereas the two penta-coordinate models 3 and 4 give the worst match. Taking all results into account – geometry, energy and EXAFS – DFT model 5 seems to be the closest representative for the structure underlying in the experimental data of Co4L1 we have so far. In this model, the six O- and N-atoms bound to the central Co-atom are aligned in a low symmetrical fashion, which might be described as quadrat-ry-pyramidal (O\(_2\)N\(_3\)H\(_*\)) with one (extra) N-atom below but close to the quadratic plane, (see Fig. 3). However, these results seemingly are in contradiction with the XANES spectrum of Co4L1, which looks like typical octahedral or trigonal-bipyramidal (i.e. high local coordination symmetry) compounds, e.g. the hexa-aqua Co[u] compound used for reference (black line in Fig. 2a).

The answer to this riddle might be the potentially underestimated electronic and steric effect of the agnostic proton in DFT model 5, which is part of the carboxylated phenyl group, see Fig. 3. Since the organic ligand system has only limited flexibility, an unoccupied coordination site can be filled by a C or metallophile contacts. AIM and NCI are complemented by the Electron Localizability Indicator (ELI-D), which dissect real-space into regions/basins of (non-) bonding electron pairs, resembling in a way the Lewis-picture of chemical bonding. An iso-surface representation is shown in Fig. S6f.† Highlighted (solid, green) are the six non-bonding d-electron ELI-D basins of the Co-atom, which altogether form a regular polyhedron in order to minimize electron-electron repulsion to the electron pairs from the electron donating ligand atoms, according to the well-known “key-lock” arrangement in transition metal chemistry.

**AIM atomic Co basin has the basic shape of a cube (typical for octahedral ligand sphere) with one edge cropped by the capping N-atom, see Fig. S6d.† The more interesting point, however, is that the shape of the basin is also flat along the Co⋯H axis, although the agnostic interaction is quite weak (only little ED accumulation on the respective cube face). This “regular shape” of the Co-atom is also visible applying the Non-Covalent Interactions Index (NCI),† which uncovers non-covalent bonding aspects of strong medium and even very weak atom-atom contacts, see Fig. S6e.† Ring-shaped blue-colored NCI basins indicate dominating covalent bonding aspects (one O, one N), whereas disc-shaped blue-colored NCI basins indicate dominating non-covalent bonding aspects (one O, three N). The agnostic Co⋯H contact is represented by a flat and extended greenish-blue colored NCI basin, being typical for weak non-covalent interactions, such as H⋯H or metallophilic contacts. AIM and NCI are complemented by the Electron Localizability Indicator (ELI-D),† which dissect real-space into regions/basins of (non-) bonding electron pairs, resembling in a way the Lewis-picture of chemical bonding.**

**Co4L1 catalyzed dioxygen reduction reaction**

The evaluation of the catalytic activity of Co4L1 towards oxygen reduction was carried out using the Fukuzumi and Guillard’s method, decamethyl-ferrocene was employed as a one electron donor, triflic (TFOH) or fluoroboric (HBF\(_4\)) acids were used as proton source, and, in their presence, O\(_2\) was set to react with a catalytic amount of Co4L1 in acetone. The occurrence of the oxygen reduction reaction was proved by the formation of decamethylferrocenium ion (Fc\(^+\)) with a characteristic absorption band at 780 nm (Fig. 4; \(\epsilon_{780} \text{nm} = 520 \text{M}^{-1} \text{cm}^{-1}\)).19,20 Notably, the rate and yield of formation of Fc\(^+\) is not significantly affected by the nature of the proton source (TFOH or HBF\(_4\); Fig. S7d†), thereby suggesting that the conjugate bases (OTf\(^-\) or BF\(_4^−\)) play no major role in controlling the efficiency of the O\(_2\)-reduction reactions. However, the concentration of Fc\(^+\) formed in the complex Co4L1-catalyzed reduction of O\(_2\) by Fc\(^+\) is dependent on the temperature at which the reactions were performed (Fig. 4 bottom, S7a–c†). At 30 °C 0.35 mM of Fc\(^+\) ion is generated in the reaction, which corresponds approximately twice that of the O\(_2\) concentration (0.18 mM). Thus, only two-electron reduction of O\(_2\) occurs at 30 °C. With decreasing temperature, the amount of Fc\(^+\) generated from O\(_2\) reduction increases, presumably because of the increasing contribution of the four-electron reduction of O\(_2\). At 25 °C the amount of Fc\(^+\) formed is 0.44 mM, which is 2.5 times that of the O\(_2\) concentration. The mechanism shifts predominantly to a four-electron reduction process at −50 °C; the amount of Fc\(^+\) gener-
ated is 0.62 mM, which represents 3.45 equiv. relative to the initial concentration of O2 (0.18 mM).

1H-NMR spectrum (Fig. 5a) of the reaction mixture of Co4L1 (0.04 mM), Fc* (3 mM), TFA (10 mM) and O2 (0.18 mM) at 25 °C in d6-acetone further confirms the change in mechanism from a predominantly 2e− reduction of O2 (to H2O2) at 0 °C to a 4e− reduction to H2O at −50 °C. The solution after the Co4L1 catalysed O2 reduction at 30 °C shows a signal at 3.88 ppm, whose position is upshifted relative to the signal at 3.93 ppm obtained for an authentic H2O2/H2O mixture (70 weight % H2O2 basis) in d6-acetone at 25 °C. Note that the signal corresponding to a H2O2/H2O mixture undergoes a downshift with increasing amounts of water in the mixture; pure water shows a signal at 4.61 ppm. Thus for a catalytic reaction at 30 °C, a >70% H2O2 concentration can be inferred. When the catalysis is performed at 25 °C the signal gets downshifted to 3.99 ppm, thereby confirming the presence of the higher amount of water as the 4e− reduction product. The resultant solution after the catalytic O2-reduction reaction at −50 °C shows a signal at 4.20 ppm, which lies between the signals at 4.44 ppm and 4.05 ppm obtained for authentic 15% and 30% H2O2/H2O mixtures, respectively. A turnover number (TON) of 28.7 during a lapse of 2000 s was determined in acetone at −50 °C. The TON decreased linearly with increasing temperature to a value of 9 at 25 °C (Fig. S8†).

**Reaction of Co4L1 with dioxygen to form 1**

An acetone solution of Co4L1, when treated with O2 saturated acetone at −50 °C, results in the formation of an orange species 1 with an intense absorption maximum λmax (εmax M−1 cm−1) centered at 464 nm (12 200 M−1 cm−1). As the temperature is increased, the absorption band at 464 nm due to 1 is decreased (Fig. 6: top one). This process is reversible in the temperature range −50 to 30 °C. The resonance Raman (rR) spectrum (Fig. 6: bottom one) of 1 in acetone-d6 displays two isotopically sensitive vibrational bands at 862 (O–O stretching mode of a peroxo ligand) and 595 cm−1 (Co–O stretching mode), which are downshifted to 808 and 561 cm−1, respectively, in 18O2 prepared samples.

XAS studies were also performed to probe the oxidation state and the coordination environment of Co in 1. The XANES spectra of 1 when compared with that of Co4L1 and other reference compounds reveals an almost complete oxidation from Co2+ to Co3+ during the transformation of Co4L1 to 1. Additionally, the edge shape of 1 shows minor altera-
tions in comparison with Co₄L₁. Bubbling O₂ into an acetone solution of Co₄L₁ (0.02 mM) produces 1 (in high yield) at −50 °C (orange, solid line). Increasing the temperature up to 25 °C produces the blue solid spectrum. After recooling to −50 °C the orange solid spectrum can be regenerated. Bottom: Resonance Raman spectra of 1-18O (red trace), 1-16O (black trace) with 514 nm laser excitation in acetone-d₆ at −40 °C. Solvent bands are marked by “blue color”.

Fig. 7 Top: Changes in the absorption band associated with the reaction of 1 (0.015 mM) with TFA (3 mM) and Fe⁺ (0.15 mM) at −50 °C; Inset: The pseudo-first-order decay of the absorption band at 464 nm as a function of time (left) and the linear dependence (right) of the pseudo-first-order rate constants (kobs) on Fe⁺ concentrations (0.15−0.38 mM) that led us to determine the second order rate constant value, k₂. Bottom: Changes in the absorption band associated with the reaction of 1 (0.015 mM) with TFA (0.75 mM) at +25 °C; inset: the pseudo-first-order decay of the absorption band at 464 nm as a function of time (left) and the linear dependence (right) of the pseudo-first-order rate constants (kobs) on TFA concentrations (0.75−2.7 mM) led us to determine the second order rate constant value, k₂.

Similarly, no reaction of 1 with TFOH was observed in the absence of Fe⁺. However, in the presence of both TFA and Fe⁺ 1 underwent fast decay, presumably by a proton-coupled electron transfer (PCET) mechanism to form water as the major product (Fig. 7 top). At 25 °C in the absence of TFA, no reduction of 1 by Fe⁺ was observed, very similar to our findings at −50 °C. However, in presence of TFA, even in the absence of Fe⁺, fast decay of 1 was observed (Fig. 7 bottom), with the release of H₂O₂ by a proton transfer (PT) mechanism.

The temperature dependence of the PT and PCET processes will be the controlling factor in determining the temperature dependence of the 4e⁻/4H⁺ vs. 2e⁻/2H⁺ reductions of dioxygen mediated by 1. We therefore compared the temperature-dependence of the PCET and PT processes of 1 at various temperatures (Fig. 7, 8 and S9†). PCET rates were determined at −50 °C, −40 °C, −30 °C and −20 °C under the condition [1] ≪ [Fe⁺] ≪ [TFA] to ensure pseudo first-order kinetics (Fig. 7 top; at these temperatures PT rates are negligible). Similarly, PT rates were determined at 20 °C, 22 °C, 25 °C, 30 °C and 32 °C under the condition [1] ≪ [TFA] (Fig. 7 bottom). PT is found to vary with temperature at a much more drastic rate relative to that of PCET, and it becomes the predominant mechanism for the reduction of 1 at temperatures >11 °C (Fig. 8a).
The faster self-decay rate \((1 \times 10^{-4} \text{ s}^{-1})\) for \(1\) vs. \(2 \times 10^{-3} \text{ s}^{-1}\) for \(1\) at 25 °C, as well as the 16 cm\(^{-1}\) downshift in the Co–O vibration energy \(\nu_{\text{Co–O}}\) for \(1\) is 595 cm\(^{-1}\) and 611 cm\(^{-1}\) for \(2\) in \(1\) relative to \(2\), is consistent with the lower stability of \(1\). Accordingly, as previously observed, the high enthalpic stability of \(2\) makes its formation at ~50 °C highly favored that leads to the complete oxygenation of \(\text{Co}_6\text{L}_2\). Complex 2 then undergoes O–O bond cleavage via a PCET mechanism to yield water as the sole product under catalytic turnover conditions. The rate constant of the reaction was found to be independent of the \(\text{O}_2\) concentration; the kinetic equation at ~50 °C for \(\text{Co}_6\text{L}_2\) is

\[
d[\text{Fc}^*]/\text{dt} = k_{\text{obs}}[\text{Co}_4\text{L}_2]\]

\[
k_{\text{obs}} = k_{\text{cat}}[\text{Fc}^*][\text{TFA}]/[\text{O}_2]
\]

where \(k_{\text{cat}}\) is the third-order rate constant for the catalytic 4e\(^–\)-reduction of \(\text{O}_2\) by \(\text{Fc}^*\) at ~50 °C and \(k_{\text{obs}}\) is the pseudo first-order rate constant. In contrast, an equilibrium binding of \(\text{O}_2\) occurs for \(\text{Co}_4\text{L}_1\), even at ~50 °C, so that the rate of the catalytic reaction shows a linear dependence on the \(\text{O}_2\) concentration (Fig. S10\(^†\)). The rate equation for \(\text{Co}_4\text{L}_1\) is

\[
d[\text{Fc}^*]/\text{dt} = k_{\text{obs}}[\text{Co}_4\text{L}_1]\]

\[
k_{\text{obs}} = k_{\text{cat}}[\text{Fc}^*][\text{TFA}]/[\text{O}_2]
\]

where \(k_{\text{cat}}\) is the fourth-order rate constant for the catalytic 4e\(^–\)-reduction of \(\text{O}_2\) by \(\text{Fc}^*\) at ~50 °C and \(k_{\text{obs}}\) is the pseudo first-order rate constant. Furthermore, \(\text{Co}_4\text{L}_1\) catalysed \(\text{O}_2\) reduction yields 15–30% \(\text{H}_2\text{O}_2\) at ~50 °C, in contrast to \(\text{Co}_6\text{L}_2\) for which no \(\text{H}_2\text{O}_2\) production could be detected at this temperature. However the rate constant of the two-electron \(\text{O}_2\) reduction at ~25 °C is a fourth-order process for both \(\text{Co}_6\text{L}_2\) and \(\text{Co}_4\text{L}_1\) (Fig. S11\(^†\)).

The constraints imposed by the stannoxane core ensure entropic instability of both \(1\) and \(2\). This is mainly because of the large reduction in the Co–Co distances that is associated with their formation. Although experimental determination of the Co–Co distances in \(\text{Co}_4\text{L}_1\), \(\text{Co}_4\text{L}_2\), \(1\) and \(2\) was not possible, approximate shortening of ~2.4 Å (from a distance of 6.82 Å in \(\text{L}_1\) to the DFT calculated distance of 4.48 Å in \(1\)) and ~7 Å (from a distance of 11.36 Å in \(\text{L}_2\) to the DFT calculated distance of 4.48 Å in \(2\)) can be predicted for dioxygen binding at \(\text{Co}_4\text{L}_1\) and \(\text{Co}_4\text{L}_2\) complexes, respectively. This would impose a large strain on the \(\mu_1,2\)-peroxo-dicobalt(III) cores in \(1\) and \(2\), which would attribute to their instability at higher temperatures upon protonation leading to the formation of \(\text{H}_2\text{O}_2\) as the major product. Thus for both \(\text{Co}_4\text{L}_1\) and \(\text{Co}_4\text{L}_2\), an equilibrium binding of \(\text{O}_2\) will take place at 25–30 °C, such that only a small portion of \(\text{Co}_4\text{L}_1\) and \(\text{Co}_4\text{L}_2\) will be converted to \(1\) and \(2\), respectively. This would also explain the experimentally observed direct correlation of the reaction rates to oxygen concentration at 25–30 °C in both cases.

In summary, the \(\text{Co}_4\text{L}_1\) complex like the previously reported \(\text{Co}_4\text{L}_2\) complex is a unique catalyst for dioxygen-reduction reaction, whereby the product selectivity can be changed from...
a predominant 4e/4H\(^+\) reduction process (to water) at \(-50^\circ\text{C}\) to a 2e\(^-/2\text{H}^+\) process at 25–30 °C. \(\mu\)-1,2-peroxo-dicobalt(n) complexes 1 and 2 are proposed as plausible reactive intermediates, which are reduced to \(\text{H}_2\text{O}\) by a PCET mechanism at \(-50^\circ\text{C}\), or to \(\text{H}_2\text{O}_2\) by a proton transfer mechanism at 25–30 °C. For both 1 and 2, the PT rates are found to vary drastically with temperature relative to the PCET rates, and PT becomes the predominant mechanism at 11 °C for 1 and at 19.5 °C for 2. The \(-10^\circ\text{C}\) reduction in the transition temperature for 1 can be attributed to its reduced stability relative to 2, as also evident from the faster self-decay rate and lower \(\nu\)(CO–O) vibration energy in 1 relative to 2. This study, therefore, underlines the importance of subtle electronic and steric changes in the reactivity of the biologically relevant metal–dioxygen intermediates, and how they can control the 2e\(^-/2\text{H}^+\) vs. 4e\(^-/4\text{H}^+\) product selectivity in catalytic dioxygen reductions.

**Conflicts of interest**

There are no conflicts to declare.

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