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## COMMUNICATION

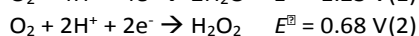
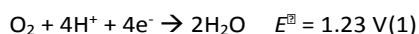
## Anion Controlled Selectivity in Oxygen Reduction Catalysed by a Dinuclear Cobalt N,O-Schiff Base Complex

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**A new dinuclear cobalt complex selectively catalyses 4e<sup>-</sup> reduction of O<sub>2</sub> to water in methanol containing acetic acid. Its TOF of 0.031 s<sup>-1</sup> and overpotential of 690 mV outperform the few previous Co N,O-chelate based catalysts for the 4e<sup>-</sup> ORR. Replacing acetic acid with NH<sub>4</sub>PF<sub>6</sub> as proton source induces a complete and unprecedented switch to the H<sub>2</sub>O<sub>2</sub> producing 2e<sup>-</sup> pathway. Mechanistic studies suggest a peroxo intermediate for both pathways, with acetate coordination/decoordination determining the destination of a key electron transfer.**

The oxygen reduction reaction (ORR) is important to biological respiration,<sup>1</sup> fuel cell technology,<sup>2</sup> metal-air batteries<sup>3</sup> and aerobic oxidations.<sup>4</sup> The ORR in acidic media can proceed via two pathways; the two-electron (2e<sup>-</sup>) pathway to generate hydrogen peroxide, or the four-electron (4e<sup>-</sup>) pathway to water (eqns 1 and 2). As it is more exergonic and does not form the corrosive and oxidising H<sub>2</sub>O<sub>2</sub>, the 4e<sup>-</sup> pathway is generally preferred in the context of fuel cells. However, there is increasing interest in electrochemical synthesis of H<sub>2</sub>O<sub>2</sub> via 2e<sup>-</sup> ORR as an alternative to the current industrial anthraquinone process,<sup>5</sup> and due to its importance to lithium-air batteries<sup>3</sup> and potential as an energy carrier.<sup>5c,6</sup>



Molecular catalysis of the ORR in acidic organic media has been studied in detail for metalloporphyrins and phthalocyanines,<sup>7</sup> and Schiff base and oxime complexes,<sup>8</sup> but biasing the catalytic system to the 4e<sup>-</sup> rather than the 2e<sup>-</sup> pathway is challenging. Methods to increase selectivity for the 4e<sup>-</sup> pathway include: using a proton-electron transport mediator (e.g. hydroquinone, quinol) to facilitate O-O bond breakage,<sup>8b,9</sup> adding proton relays

/ pendant bases to facilitate protonation of bound oxygen species,<sup>8d,10</sup> or using Brønsted scaling relationships to disfavour H<sub>2</sub>O<sub>2</sub> production.<sup>11</sup> Using dinuclear complexes, such as “hangman” porphyrins, to favour the 4e<sup>-</sup> pathway has also shown success.<sup>12-16</sup> Yet, for Co(II) salen-type complexes, which generally only catalyse the 2e<sup>-</sup> pathway, dinuclear approaches to the ORR are to our knowledge unexplored.

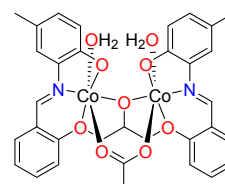


Fig. 1 Structure of the dinuclear Schiff base ORR catalyst [Co<sub>2</sub>(MeBSIP)(OAc)(H<sub>2</sub>O)<sub>2</sub>] (**2**)

Herein, we show that a novel, easily accessible dinuclear Co(II) complex with a salen-like N,O chelating unit (**2**, Fig. 1) catalyses the 4e<sup>-</sup> ORR with high (>90%) selectivity, and better turnover frequency (TOF) and overpotential metrics than comparable mononuclear systems. Moreover, changing the anions in solution (from AcO<sup>-</sup> to non-coordinating PF<sub>6</sub><sup>-</sup>) enables a complete switch to the 2e<sup>-</sup> pathway, independent of the pK<sub>a</sub> effects that control selectivity in Co(TPP) catalysts.<sup>11</sup> While anion / co-ligand effects are known in catalysis,<sup>17</sup> they are not previously reported as a way to control the pathway in the ORR.

Compound **2**, [Co<sub>2</sub>(MeBSIP)(OAc)(H<sub>2</sub>O)<sub>2</sub>] (H<sub>3</sub>MeBSIP = 2,2'-[(2-hydroxy-1,3-propanediyl)bis(oxy-2-benzylideneamino)]di-[4-methylphenol], Fig. 1) was synthesised in two steps (see ESI for full details) *via* dialdehyde precursor 2,2'-[(2-hydroxy-1,3-propanediyl)bis(oxy)]bis-benzaldehyde (**1**), which was reacted with cobalt(II) acetate and 2-amino-4-methylphenol to produce **2** by a templated imine condensation. Compound **2** has been characterised by ESI mass spectrometry, CHN elemental analysis, and FTIR (Fig. S1). CHN is consistent with the presence of two coordinated H<sub>2</sub>O, IR indicates an imine stretch and also a bridging acetate coordination mode (ν = 1572 cm<sup>-1</sup>), while MS detects a doubly charged ion at *m/z* = 625.066 consistent with loss of acetate and water ligands and formation of the dimer,

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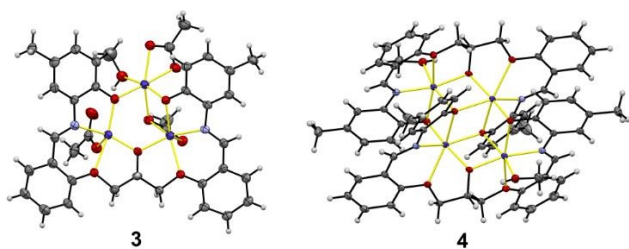
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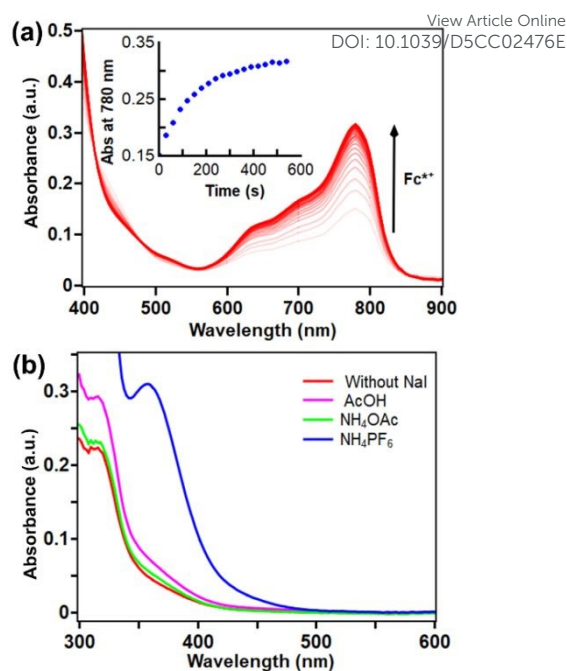




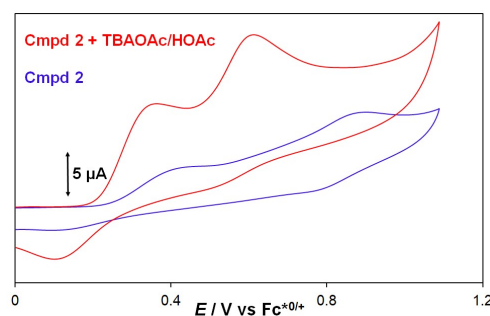
**Fig. 2** X-ray crystal structures of **3**, and the  $[\text{Co}_4(\text{MeBSIP})_2(\text{MeOH})_2]^{2+}$  complex cation in **4**. Thermal ellipsoids are at the 50% probability level, C is grey; N, blue; O, red; Co, purple, H atoms are white spheres with arbitrary radii. Coordinate bonds are shown in yellow.

$[\text{Co}_4(\text{MeBSIP})_4]^{2+}$ . X-ray quality crystals of **2** could not be obtained, but two structures based on the  $\{\text{Co}_2\text{BSIP}\}$  unit have been solved (Fig. 2; Table S1, Fig. S2 and S3, ESI). Trinuclear  $[\text{Co}_3(\text{MeBSIP})(\text{OAc})_3(\text{MeOH})]$  (**3**) forms in the presence of excess  $\text{Co}(\text{OAc})_2$ : the third Co occupies a coordination pocket defined by the two phenoxo groups, with its coordination sphere completed by acetate and methanol ligands. Defect cubane  $[\text{Co}_4(\text{MeBSIP})_2(\text{MeOH})_2](\text{BF}_4)_2$  (**4**) was isolated by adding  $\text{NaBF}_4$  to the **2** reaction mixture, and has alkoxo-bridged  $[\text{Co}_2(\text{MeBSIP})]$  units linked by formation of  $\mu_2$  and  $\mu_3$  phenolato bridges. Compounds **3** and **4** support the proposed structure of **2**, by showing  $\{\text{Co}_2\}$  units coordinated to MeBSIP through imine, ether and phenolate groups and a bridging alkoxo.

The strong bridging acetate IR signal of **2** supports (Fig. S3) existence of **2** as a  $\{\text{Co}_2\}$  rather than  $\{\text{Co}_4\}$  structure, as the  $[\text{Co}_4(\text{MeBSIP})_2]^{2+}$  unit in **4** cannot accommodate bridging acetate ligands. To further support the structure of **2**, powder XPS measurements were obtained (Fig. S4, ESI), which were consistent with a Co(II) complex containing BSIP and acetate ligands, moreover, distinct low temperature solid-state EPR spectra were obtained for the three compounds (Fig. S5, ESI). Solution equilibria likely occur between the three species, but these must be slow, as assessment of the catalytic properties of **2** to **4** for  $\text{O}_2$  reduction reveals stark differences. The three compounds were assayed for activity towards  $\text{O}_2$  reduction in air saturated methanol, buffered by TBAOAc/HOAc, with decamethylferrocene ( $\text{Fc}^*$ ) as a stoichiometric reductant, with overall compositions such that  $[\text{AcOH}] > [\text{Fc}^*] \approx [\text{O}_2] \gg [\text{Catalyst}]$ .  $\text{Fc}^*$ , through the absorption of  $\text{Fc}^{*+}$  at 780 nm, also provides a spectrophotometric probe to monitor reaction progress.<sup>13b,18</sup> For **2**, (Fig. 3, Figs S6–S8, ESI) rapid emergence of absorption at 780 nm over 10 minutes indicates that **2** catalyses oxidation of  $\text{Fc}^*$  to  $\text{Fc}^{*+}$ , by reducing  $\text{O}_2$ . In the absence of **2**, the increase in  $[\text{Fc}^*]$  over the same time period is *ca.* 20× smaller (Fig. S11). Iodometric titration with  $\text{NaI}$  (Fig. 3), which detects  $\text{H}_2\text{O}_2$  through oxidation of  $\text{I}^-$  to  $\text{I}_3^-$ , shows only a small spectral change consistent with *ca.* 10% of the  $\text{O}_2$  being converted to  $\text{H}_2\text{O}_2$  and thus a selectivity of around 90% for the  $4e^-$  pathway to  $\text{H}_2\text{O}$ . Solubilities of **3** and **4** are poor in MeOH, but adequate concentrations (*ca.* 20  $\mu\text{M}$ ) could be achieved to show that **4** has almost no activity, above the baseline, slow  $2e^-$  reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}_2$  by  $\text{Fc}^*$ , while compound **3** shows around 1/3 of the activity of **2** (Figs S9–S11, ESI). This may be due to dissociation of the third Co centre, releasing active species **2**. However, aging solutions of **3** and **4** in buffer does not increase activity.



**Fig. 3** (a) Evolution of the 780 nm absorption from  $\text{Fc}^{*+}$  for a solution of 20  $\mu\text{M}$  **2**, 20 mM  $\text{AcOH}/[\text{NBu}_4][\text{OAc}]$  and 1 mM  $\text{Fc}^*$  in air saturated MeOH. Inset: 780 nm absorbance vs time. (b) Post-reaction iodometric titrations in MeCN for proton sources  $\text{AcOH}$ , (magenta)  $\text{NH}_4\text{PF}_6$  (blue),  $\text{NH}_4\text{OAc}$  (green). 361 nm maxima are due to absorption by  $\text{I}_3^-$ .



**Fig. 4** Cyclic voltammetry of **2** (1 mM) before (blue) and after (red) addition of  $\text{AcOH}/\text{TBAOAc}$  (25 mM). MeOH, 50 mM  $\text{TBAClO}_4$ , glassy carbon electrode, 100  $\text{mV s}^{-1}$ .

A turnover frequency (TOF) for **2** for  $\text{O}_2$  production can be estimated at  $0.031 \text{ s}^{-1}$ , with initial concentrations of  $[\text{2}] = 20 \mu\text{M}$ ,  $[\text{AcOH}/\text{TBAOAc}] = 16 \text{ mM}$ , and  $[\text{Fc}^*] = 1 \text{ mM}$ , based on the initial rate of  $\text{Fc}^*$  consumption adjusted for reaction selectivity (see ESI). As ORR catalytic rates commonly show a strong dependence on overpotential, electrochemical measurements were used to evaluate the redox potentials of **2** (Fig. 4) and further underline (Fig. S12, ESI) that the three species remain distinct in solution. The cyclic voltammogram of **2** in MeOH (50 mM  $\text{TBAClO}_4$ , Fig. 4), shows two pseudo-reversible waves at  $E_{1/2} \pm 0.27 \text{ V}$  ( $\Delta E = 300 \text{ mV}$ ) and  $0.83 \text{ V}$  ( $\Delta E = 120 \text{ mV}$ ) vs  $\text{Fc}^{*0/+}$ . Respectively, these are assigned to the  $\text{Co}^{\text{II}}\text{Co}^{\text{II}}/\text{Co}^{\text{III}}\text{Co}^{\text{II}}$  ( $[\text{2}]^{0/+}$ ) and  $\text{Co}^{\text{III}}\text{Co}^{\text{II}}/\text{Co}^{\text{III}}\text{Co}^{\text{III}}$  ( $[\text{2}]^{+/2+}$ ) couples, the large peak separation of the  $[\text{2}]^{0/+}$  process resulting from the reorganisation energy associated with a redox coupled spin crossover ( $\text{HS-Co}^{\text{II}}\text{HS-Co}^{\text{II}}/\text{LS-Co}^{\text{III}}\text{HS-Co}^{\text{II}}$ ). The smaller  $\Delta E$  for  $[\text{2}]^{+/2+}$  suggests that the HS state of the second Co is stabilised as previously proposed for dinuclear cobalt complexes.<sup>19</sup> Adding  $\text{AcOH}/\text{TBAOAc}$ , to



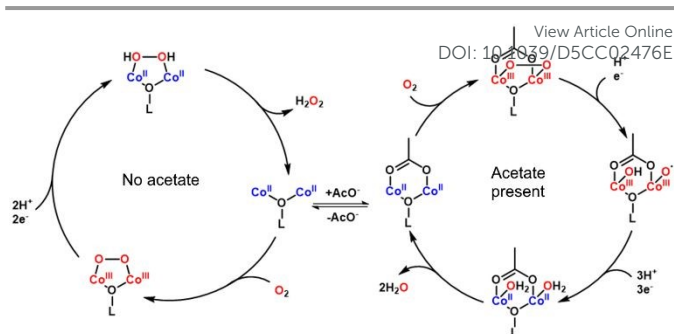
recreate the conditions used in the  $\text{Fc}^*$  driven ORR (Fig. 4) substantially increases the peak currents and shifts the waves to  $E_{1/2} + 0.23$  ( $\Delta E = 260$  mV) and  $0.56$  V ( $\Delta E = 100$  mV). Increased peak currents likely result from higher conductivity due to increased total electrolyte concentration – similar behaviour is observed for  $\text{Fc}^{*0/+}$  – while the negative shift in the  $[\mathbf{2}]^{+/2+}$  redox potential implies an electrochemical anation reaction producing  $[\mathbf{2}(\text{OAc})]$  occurs on the first oxidation, the lowered charge facilitating the second process.

Like many ORR catalysts, the electrochemical response of  $\mathbf{2}$  to air is too weak to distinguish an electrocatalytic wave, but the overpotential for molecular ORR catalysts ( $\eta_{\text{eff}}$ ) can be estimated by the difference between the thermodynamic cell potential under the non-standard catalytic conditions, and the  $E_{1/2}$  of the most negative catalyst redox event in the catalytic cycle: i.e. the  $[\mathbf{2}]^{0/+}$  couple. The  $E_{\text{O}_2/\text{H}_2\text{O}}$  in 25 mM AcOH/TBAOAc in methanol can be estimated at  $+0.92$  V vs  $\text{Fc}^{*0/+}$ ,<sup>11</sup> giving an overpotential for  $\mathbf{2}$  of 690 mV. For this overpotential, the TOF ( $0.031 \text{ s}^{-1}$ ) obtained is substantially faster than can generally be projected for Fe ( $<10^{-5}$ )<sup>8a</sup> porphyrins, or Co pyridyl derivatives ( $<<10^{-2}$ ) for the  $4e^-$  process.<sup>8d,e</sup> The literature lacks the data to enable detailed comparison with other dinuclear Co catalysts, but looking at metrics for molecular  $4e^-$  ORR catalysts in general,  $\mathbf{2}$  has a high selectivity and high TOF for its overpotential, although it should be noted that mononuclear Co complexes with pendant quinols have achieved better rate and overpotential combinations.<sup>9</sup>

Further chemically driven ORR experiments revealed a first-order dependence on  $[\mathbf{2}]$  and  $[\text{Fc}^*]$ , but a zero-order dependence on  $[\text{O}_2]$  between 2 and 10 mM (Fig.s S17-S20, ESI). The latter is consistent with spectroscopic and electrochemical evidence for  $\text{O}_2$  binding by  $\mathbf{2}$  (Fig.s S15, S16, S26-S30, ESI), and  $[\text{O}_2]$  being  $\geq 100\times$  greater than  $[\mathbf{2}]$  (20  $\mu\text{M}$ ), so nearly all of the  $\mathbf{2}$  is  $\text{O}_2$  bound. The former indicate a rate-determining step involving one equivalent of  $\mathbf{2}$  and one electron, likely a slow electron transfer (ET) step that facilitates breakage of the strong O-O bond. Dependence on acid concentration is more complex: increasing  $[\text{AcOH}]$  in the absence of buffer *decreases* rate (Fig. S21), but increasing buffer (AcOH/TBAOAc) concentration increases rate with a near first-order dependence (Fig. S22). At constant buffer concentration, a second-order catalytic rate equation can be constructed (eqn. 1).

$$\frac{d[\text{Fc}^{*+}]}{dt} = k_{\text{cat}}[\mathbf{2}][\text{Fc}^*] \quad (1)$$

Considering the rate equation, alongside electrochemical measurements and studies of related catalysts from the literature, we propose a mechanism in which water ligands dissociate from  $\mathbf{2}$ , and  $\text{O}_2$  is spontaneously and reversibly bound in an oxidative addition producing a peroxo-bridged  $\text{Co}^{\text{III}}\text{Co}^{\text{III}}$  intermediate – evidenced by loss of paramagnetism in both NMR and EPR measurements (Fig.s S26-S30, ESI). Then, electron transfer (ET) to and protonation of this peroxo species results in an oxyl radical-hydroxo species which is quickly quenched by three protons and reducing equivalents to regenerate  $\mathbf{2}$  (Scheme 1, right). The dependence on AcOH and  $\text{AcO}^-$  is complicated, because while protons are needed to complete



**Scheme 1** Proposed mechanisms. **Left:** Two-electron reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}_2$  by  $\mathbf{2}$  in the absence of  $\text{AcO}^-$ . **Right:** Four-electron reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}$  by  $\mathbf{2}$  with  $\text{AcO}^-$  present.

the cycle, protonation of the catalyst appears to induce positive shifts in the  $[\mathbf{2}]^{0/+}$  redox potential (Fig. S13, ESI), while coordination of acetate may block substrate access.

The anion effect was further probed by changing proton source to  $\text{NH}_4\text{PF}_6$  ( $\text{pK}_a$  in MeOH = 10.78, vs 9.8 for AcOH). Remarkably, this flips the selectivity almost entirely to the  $2e^-$  pathway, with iodometric titration revealing 93% of the theoretical  $[\text{H}_2\text{O}_2]$ . To test whether this change resulted from  $\text{pK}_a$  or coordination, catalysis was performed with  $\text{NH}_4\text{OAc}$  ( $\text{pK}_a = 10.78$ ) – returning the system to the  $4e^-$  pathway with 97%  $\text{H}_2\text{O}$  selectivity (Fig. 3). This result indicates that  $\text{AcO}^-$  binding is crucial to the  $4e^-$  pathway. There are two possible explanations for this: (i) without excess  $\text{AcO}^-$  in solution, decooordination of the acetate ligand destabilises the dicobalt binding site for  $\text{O}_2$ , resulting in two, connected mono-Co salen catalysts that operate independently: mono-Co salens favour the  $2e^-$  pathway via superoxo species; or (ii) the dicobalt  $\text{O}_2$  binding site is retained, but loss of  $\text{AcO}^-$  makes the  $\text{Co}(\text{III})$  centres more electron poor, so that electron transfer (ET) to Co and release of peroxide becomes more favourable than ET to the peroxo ligand and cleavage of the O-O bond.

Neither (i) nor (ii) can be definitively ruled out, but electrochemical, kinetic and spectroscopic evidence point towards (ii) (Scheme 1, left). Cyclic voltammetry in the presence of  $\text{NH}_4\text{PF}_6$  (Figure S14, ESI) shows that the two redox processes of  $\mathbf{2}$  are still present, indicating communication between the two Co centres (i.e. a dinuclear binding site), but shifted to more positive potential by *ca.* 80 mV vs the acetate medium. A two-site catalyst could be expected to have a lower reaction order than  $\text{Fc}^*$  or the proton source, but similar rate vs concentration dependencies are seen for all of these species (Figure S23-S25). EPR under air at room temperature, 50 K and 10 K shows no evidence of superoxo species, but the  $\text{Co}^{\text{II}}$  signals disappear in the low temperature measurements, consistent with formation of a peroxo-bridged dicobalt(III) complex. This suggests a catalytic cycle of the type shown in Scheme 1, with the rate-determining step being a final PCET step to release  $\text{H}_2\text{O}_2$ . At the estimated overpotential of 80 mV, the TOF ( $0.125 \text{ s}^{-1}$ ) obtained for the  $2e^-$  process is *ca.* 5x higher than expected for mononuclear  $\text{Co}^{\text{II}}$  salens,<sup>7a</sup> which proceed via a  $\text{Co}^{\text{III}}$  superoxo intermediate, indicating an advantage for the dinuclear structure and consistent with a different mechanistic pathway.

In summary, we have designed and synthesised a novel dinuclear molecular catalyst with  $>90\%$  selectivity for  $4e^-$





reduction of O<sub>2</sub> in acetate buffers, and >90% selectivity for the 2e<sup>-</sup> pathway with non-coordinating PF<sub>6</sub><sup>-</sup>. This high selectivity is combined with highly competitive TOFs (0.031 / 0.125 s<sup>-1</sup>) relative to overpotential (690 / 80 mV) for both processes. Both routes appear to involve a dicobalt(III) peroxo intermediate, with coordination/decoordination of acetate modulating the proton and electron transfer properties. Future studies will establish a  $\eta_{\text{eff}}$  vs. Log(TOF) trend between similar catalysts bearing electron withdrawing and donating substituents.

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## Data availability

Data supporting this article are presented in the ESI and are available at DOI:10.17635/Lancaster/researchdata/731. Crystallographic data for **3** and **4** have been deposited at the CCDC, deposition numbers 2447929 and 2447930.

## Conflicts of interest

There are no conflicts to declare

## Notes and references

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