Dioxygen reduction catalyzed by dicobalt Pacman complexes

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The development of fuel cell technologies for automotive use in particular is integral to clean and sustainable energy generation, and relies on catalysts to carry out fundamental chemical redox reactions at the electrodes. At present, the four-electron reduction of dioxygen to water that occurs at the cathode is the most problematic as it is catalysed by expensive Pt metal that requires considerable overpotentials and has limited long-term stability. As such, there is increasing effort to find cheaper and more durable alternatives which requires a fundamental understanding of the mechanism of this reaction.

Molecular metal complexes often provide great insight into the detail of a chemical reaction as geometric and electronic structures can be elucidated in solution and the solid state. In particular, dicobalt cofacial or Pacman diporphyrins have proved extremely efficient as catalysts for selective dioxygen reduction, and have allowed many facets of this reaction to be characterised (Fig. 1). In these complexes, the coordination geometries of the metals and their relative positions are predetermined by the ligand design, and this feature has been shown to be critical to the selectivity of the reduction reaction.

As an alternative, we have developed the metallation chemistry of new, straightforwardly-prepared macrocyclic ligand \( \text{H}_2L \) (Fig. 1) and have found that its metal complexes adopt double-pillared Pacman structural geometries, both in solution and in the solid state; as such, these complexes are similar to cofacial diporphyrins. A structural survey of a series of \( \text{Pd}_2(L) \) complexes in which the ligand periphery was varied showed that this bimetallic microenvironment is less flexible than in the porphyrinic analogues, which would likely have a significant effect on the chemistry of these compounds.

The chemistry of the dicobalt complexes \( \text{Co}_2(L) \) has been particularly interesting. The reaction between \( \text{Co}_3(L) \) and air was found to form a 90:10 mixture of two related complexes, the peroxo complex \( \text{Co}_2(O_2)(L) \) and the one-electron oxidised superoxo cation \( \text{Co}_2(O_2)(L)^+ \). The solid state structure of the pyridine adduct of the peroxo complex was determined and showed that the O\( _2 \) was bound between the two metals in the cleft and adopted a zigzag “Pauling” bonding mode. This was the first time that the structure of any dicobalt Pacman complex containing a reduced form of O\( _2 \) had been described. The solid state structure of the acetonitrile adduct of \( \text{Co}_2(O_2)(L) \) was also determined, and showed a 0.02 Å elongation of the O-O distance (1.389 Å) in the solid state (Fig. 2). However, DFT calculations indicated that the O-O bond distance was not a good indicator of the degree of formal reduction of O\( _2 \) and the apparent similarity in the O-O distance was more likely to be a consequence of the constrained cleft environment.

The catalytic chemistry of these complexes was studied in acid solution, and showed that while they acted as catalysts for the four-electron reduction of dioxygen to water, the turnover number was low. It was reasoned that this is due to the low concentration of the catalytically active species, the superoxo cation \( \text{Co}_2(O_2)(L)^+ \) and the formation of bridged hydroxyl complexes such as \( \text{Co}_2(\text{OH})(L)^+ \), one of which was characterised structurally (Fig. 2).

At present, we are investigating ligand modifications that inhibit the formation of mono-atom bridged compounds through the use of sterically hindered meso-substituents or elongated aryl hinge groups, and have recently found that \( \text{M}_2(L) \) complexes of these new ligands have very different bimetallic cleft environments in the solid state.

The characterisation of these metal complexes in the solid state by X-ray crystallography allows us to determine key parameters such as M–M separation, M-L and O-O bond distances, and the overall shape of the complex (i.e. Pacman or not?). This information is invaluable to us in constructing structure-activity relationships and to assist in the design new ligands that build on these features. Access to the Cambridge Crystallographic Database is important as it allows us to compare structural data accurately and efficiently in ConQuest, in particular using defined bond distances or short contacts such as hydrogen bonding interactions, to manipulate known chemical structures using tools such as Mercury, and to analyse large series of bond distances in Vista to determine ranges and means for selected bonds e.g. peroxo \( \text{O}_2^- \) versus superoxo \( \text{O}_2^- \).