

Greenhouse Gas Emission Reductions: Development of Energy Efficient Catalysts for Post Combustion Capture of CO₂, A novel lower cost method for CO₂ capture.

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ABSTRACT

Anthropogenic CO₂ production is a major contributor to atmospheric CO₂ levels that have increased from around 250 ppm at the start of the industrial revolution to around 380 ppm currently. Projections by the International Panel on Climate Change predict that a business as usual (BAU) scenario will produce a level of 850 ppm by 2050 and will result in serious climate extremes (melting polar ice, sea level increases, and disruption of ocean currents). Reductions from this projected level, could be achieved from efficiencies, by switching to generation of energy from renewable or non-carbon sources, (solar, wind, hydro or nuclear generation), however fossil fuels will still be essential to maintain projected energy demands. To achieve the emission reductions desired, carbon capture and storage will be required as the major technology that must be implemented. While new power plants may use the newer technologies that facilitate CO₂ capture (decarbonisation with pre-combustion capture, oxy-fuels), retrofitting of existing conventional power generating plants is more problematical.

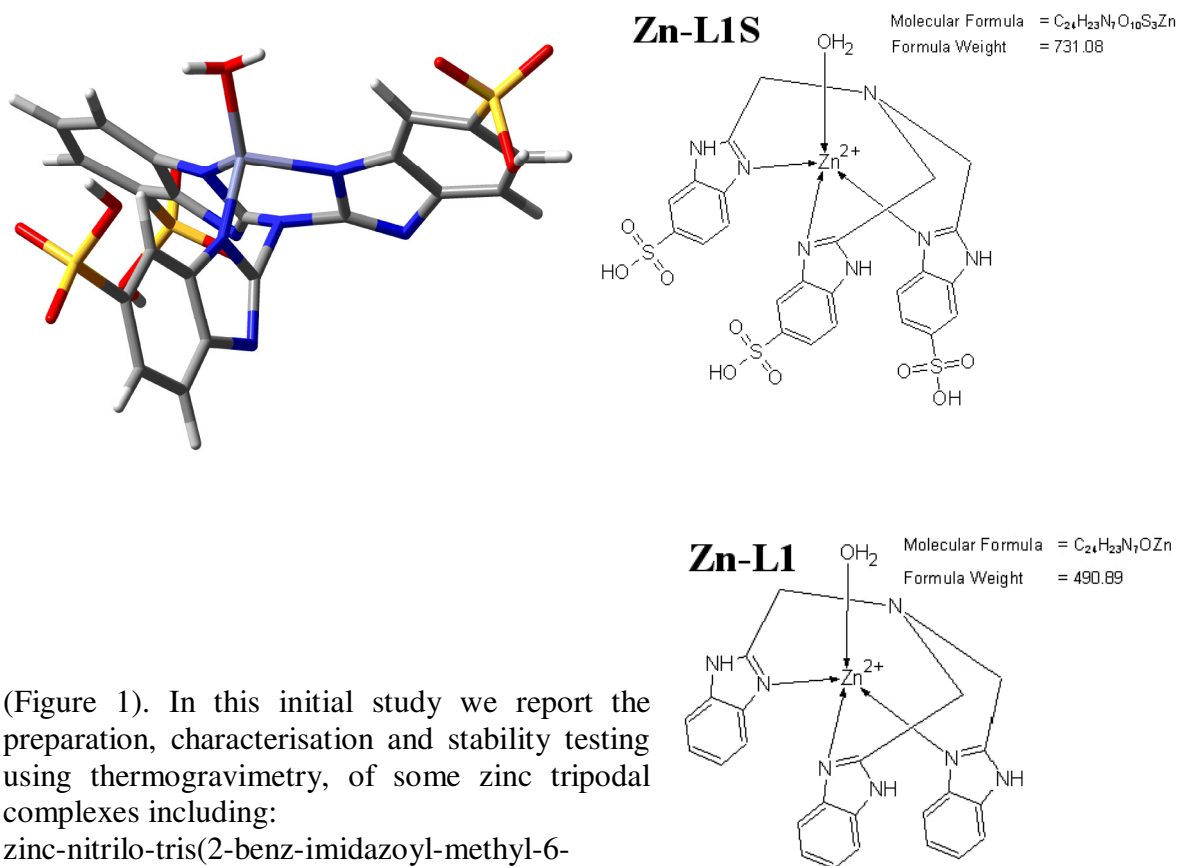
The flue gases from conventional industrial plants using carbon based fuels typically contain 4 - 14% carbon dioxide, which must be concentrated by capture to allow compression for storage. At present, the best method for capture - used in the purification of natural gas - is the chemical absorption–stripping cycle of CO₂ with an amine solvent - usually monoethanolamine (MEA). This mature technology is expensive on the large scale (around \$40-\$80US /tonne of CO₂ captured) and retrofitting to existing coal burning plants is uneconomic, reducing efficiencies to as low as 10%. Disadvantages of MEA include its corrosive properties, requirements to replenish evaporative losses, chemical and thermal degradation (particularly by SO_x, NO_x and unburnt oxygen) occurring in the absorption-stripping cycle. A further major disadvantage of MEA is the energy cost in the stripping procedure requiring steam at temperatures of around 120 °C.

Carbonic anhydrases, (CA), are widely occurring zinc metallo-proteins (enzymes) that catalyse reversibly the hydration and dehydration of CO₂ at ambient temperatures in living organisms. Several authors have suggested using CA in a new carbon capture system, but the enzyme is costly to produce, has a high molecular weight of 30,000 g/mol (limiting molar concentration) and it is only stable below 85 °C. Nevertheless, Trachtenberg proposed a system, using CA in conjunction with a thin liquid membrane, with a projected cost reduction to \$26US /tonne.

We have identified a class of metal complexes that mimic CA, apparently not subject to the disadvantages of stability, cost, size limitation or concentration that apply to CA. The catalytic process in both CA and the biomimetic metal complexes proceeds by hydration of CO₂ to bicarbonate followed by reverse dehydration (driven by pH change) of the bicarbonate to regenerate CO₂. These inorganic catalysts, are stable at high temperatures, operate over a wide pH range, and show fast rates of catalysis that are comparable with CA

on a weight basis, and promise affordable technology that will allow CCS retrofitting to existing power stations.

Figure 1: Zinc-L1 tripod: Zinc-tris-(2-benzimidazolmethyl)-amine; and zinc-L1S tripod: (Zn-Nitrilo-tris(2-benzimidazolyl) methyl-6-sulfonic acid)



(Figure 1). In this initial study we report the preparation, characterisation and stability testing using thermogravimetry, of some zinc tripod complexes including:

zinc-nitrilo-tris(2-benz-imidazolyl-methyl-6-sulfonic acid), (zinc-L1S), and zinc-tris(2-benzimidazolmethyl)-amine, (zinc-L1).

Further studies are in progress to immobilize the complexes onto polymer surfaces and within polymer membranes or gels, to form heterogeneous catalysts with improved stability and longevity in industrial plant operations.

CONCLUSIONS:

- Initial studies of zinc complexes show that a CO₂ capture system in water is feasible and will enable reduction of the energy penalty and other disadvantages in the amine solvents.
- The initial rates of dehydration that can be achieved by using the zinc catalysts are less than those of the fast CA enzyme, but can be achieved at moderate temperatures and around neutral pH, at a rate comparable with that of amine systems.
- The zinc catalysts are stable at over 200 °C compared with the CA enzyme which is denatured (becomes inactive) at temperatures just above 80 °C.
- The molecular weight of the Bovine CA enzyme is around 30,000g/mol compared with only 700g/mol for the complex ZnL1S. On a gram basis therefore the complex ZnL1S (dehydration rate (k_{cat}) around 800 is equivalent to the Bovine CA (k_{cat}) around 35,000.

Key Words: bicarbonate dehydration; carbonic anhydrase; CO₂ capture; catalysts; catalytic absorption; catalytic desorption; CO₂ hydration; post combustion capture; zinc complex.

