Nucleophile assisted carbon dioxide fixation for a cleaner environment

Shaun Redgard and Andreas Roodt

Department of Inorganic Chemistry, University of the Free State, Bloemfontein 9300, South Africa Email of communicating shaunredgard@icloud.com

With carbon dioxide (CO_2) reaching a peak concentration of 416 ppm in 2019 and still increasing yearly, there still has been no viable option to reduce the CO_2 concentrations in the atmosphere. This is in part due to the relatively inert nature of CO_2. However, the biomimetic investigation of plants, specifically CAM (Crassulacean Acid Metabolism) plants (Such as cacti and succulents), illustrate how CO_2 may be converted and stored [1]. The biomimetic approach can therefore aid in discovering an approach which may help overcome the energy and financial barrier for carbon capture and sequestration (CSS).

The amidines and guanidines are two classes of organic nitrogen bases that can activate CO_2 and have been used in switchable ionic liquids (SWILs) to store CO_2 and as cocatalysts or ligands in metal catalyzed reactions [2]. Furthermore, 2,2'-bipyrdine ligands have also shown promise in catalytic reactions of CO_2 [3].

The focal points to be discussed in this presentation are CO_2 and its uptake cycle in *crassula ovata* succulents (Fig.1(a)). Thereafter, the synthesized rhodium metal complexes, which contain 1,5-cyclooctadiene (COD) and the nitrogen bases as ligands, will be discussed along with characterization by single-crystal x-ray diffraction (SC-XRD). Special focus will be given to the influence the ligands have on the coordinated COD which "mimics" the Venus fly-trap plant, illustrated in Fig. 1(b-d), and the related kinetic studies by a neutral ligand to replicate CO_2 [4]. Interestingly, the results from the kinetics showed that the forward reaction rate (k_1) for the amidine-containing rhodium complex was $k_1 = 2.16 \times 10^3$ $M^{-1}s^{-1}$ with a half-life of 321 ms and **ten**-times faster for the rhodium complex containing the guanidine ligand. This can be seen to correlate with the change in angles (Fig. 1(c,d)) of the COD.

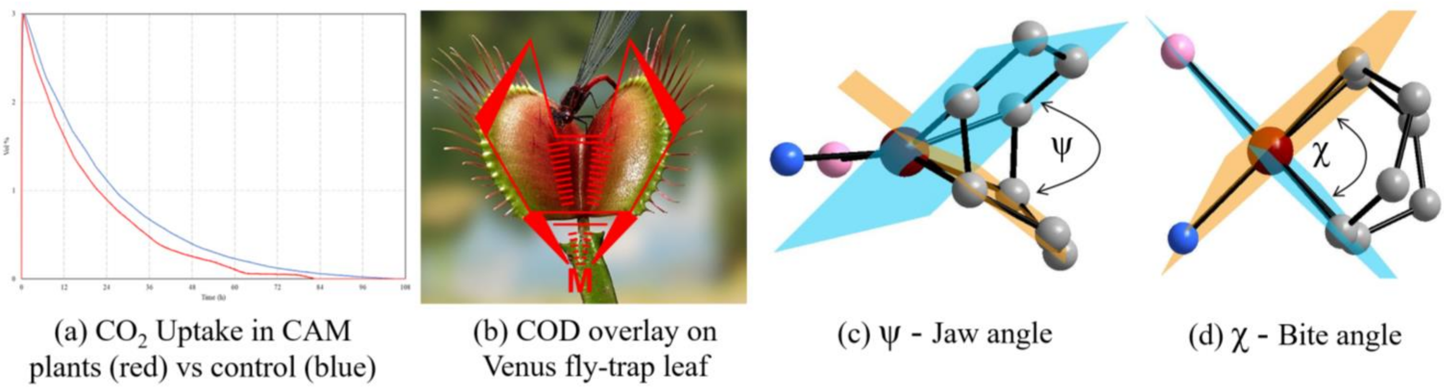

Figure 1. (a) Measured CO_2 uptake in 1 m^3 boxes between six *crassula ovata* succulents and an empty control. (b) The structural overlay of COD, coordinated to a metal centre, onto a Venus fly-trap leaf. The definitions describing the geometry of the COD ligand in relation to the Venus fly-trap conformation: (c) ψ – dihedral angle between the two planes through the four alkane carbon fragments, (d) χ – dihedral angle between the two planes through the two alkene moiety-metal atoms.

In addition to the above, five–coordinate platinum group metal complexes containing COD, a methyl/ phenyl group and various 2,2'-bipyridine ligands that have been isolated and characterized will be discussed in a similar fashion to the Rh-COD complexes [5]. An evaluation and comparison of the COD angles will illustrate the importance that crystallography has on understanding molecular structures and kinetics.

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