

# An FT-IR study of manganese dimers with carboxylate donors in high oxidation states – Influence of coordination geometry on the COO stretching frequencies and consequences for the Mn<sub>4</sub>Ca cluster of Photosystem II.

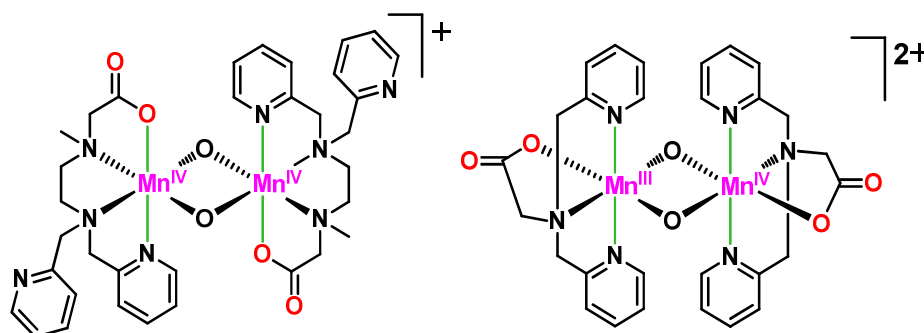
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Carboxylate donors are a reoccurring theme in the active site of a number of manganese containing redox active enzymes, e.g. Mn-catalases and the oxygen evolving complex in PSII. FT-IR is a powerful spectroscopic tool to follow changes in the coordination environment of carboxylates. Many FT-IR studies of PSII and PSII-mutants have been reported but there are surprisingly few clear results about the ligation of specific amino acid residues with carboxylate groups to the manganese ions in the active site.<sup>1</sup>

A large number of synthetic manganese complexes incorporating carboxylate ligands, aiming at mimicking either functional or spectroscopical aspects of PSII have been reported. However, only a few complexes have been characterized with FT-IR spectroscopy in multiple oxidation states and those feature only bridging carboxylates.<sup>2</sup>

We have obtained FT-IR data for the asymmetric and the symmetric carboxylate stretches for two well characterized manganese complexes with monodentate carboxylate donors (**1–2**). The complexes have subtle differences in their coordination environment; in **1**, the carboxylate moieties are coordinated perpendicular to the Mn-(μ-O)<sub>2</sub>-Mn plane, while in **2** the carboxylates are coordinated in the Mn-(μ-O)<sub>2</sub>-Mn plane.



The absolute and differential FT-IR spectra in the Mn<sub>2</sub><sup>(IV,IV)</sup>, Mn<sub>2</sub><sup>(III,IV)</sup>, and Mn<sub>2</sub><sup>(III,III)</sup> oxidation states of both complexes have been obtained. For the monodentate carboxylates the asymmetric and symmetric stretching frequencies are shifting towards each other with 50–150 cm<sup>-1</sup> per one electron reduction. In contrast, for bridging carboxylates the stretching frequencies shift away from each other upon reduction of the manganese ions and the shifts reported are much smaller.<sup>2</sup>

Consequences for the Mn<sub>4</sub>Ca cluster will be discussed, especially for the S<sub>1</sub>→S<sub>2</sub> state transition, where one manganese(III) ion is oxidized and the overall charge of the cluster is increased by +1.

- (1) (a) Noguchi, T. *Photosyn. Res.* **2007**, *91*, 59-69. (b) Debus, R. J. *Coord. Chem. Rev.* **2008**, *252*, 244-258.
- (2) (a) Wieghardt, K. *et al.*, *J. Chem. Soc., Chem. Commun.* **1985**, 347-349. (b) Wieghardt, K., *et al.*, *Angew. Chem. Int. Ed.* **1986**, *25*, 1030-1031. (c) Wieghardt, K.; *et al.*, *J. Am. Chem. Soc.* **1988**, *110*, 7398-7411.