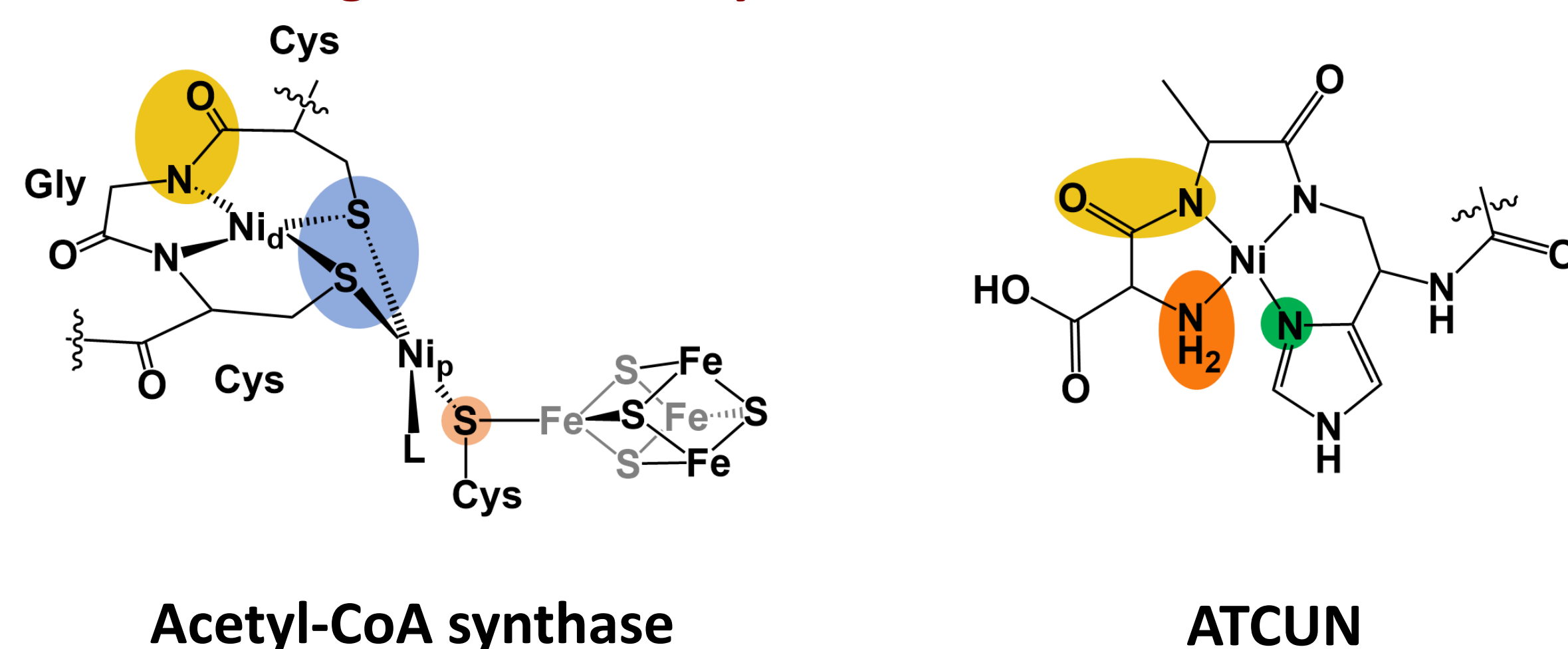


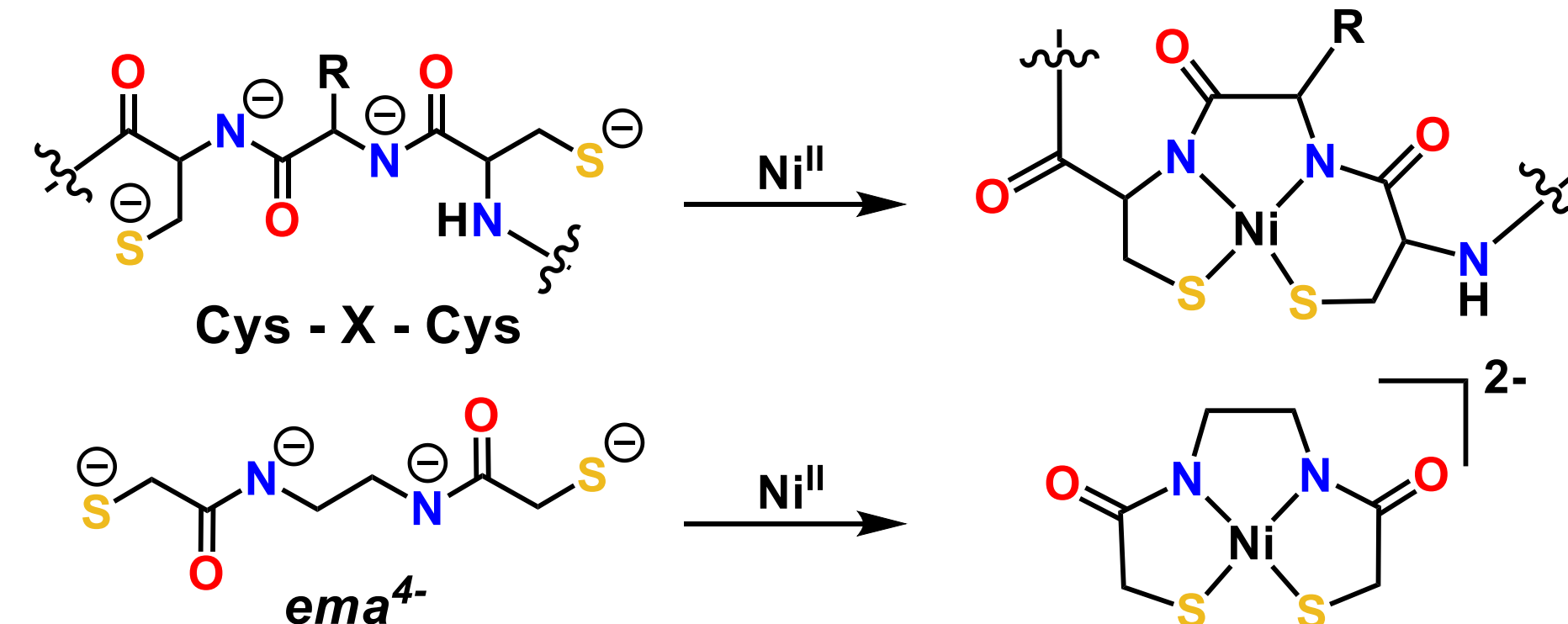


Background: metal binding sites to peptides

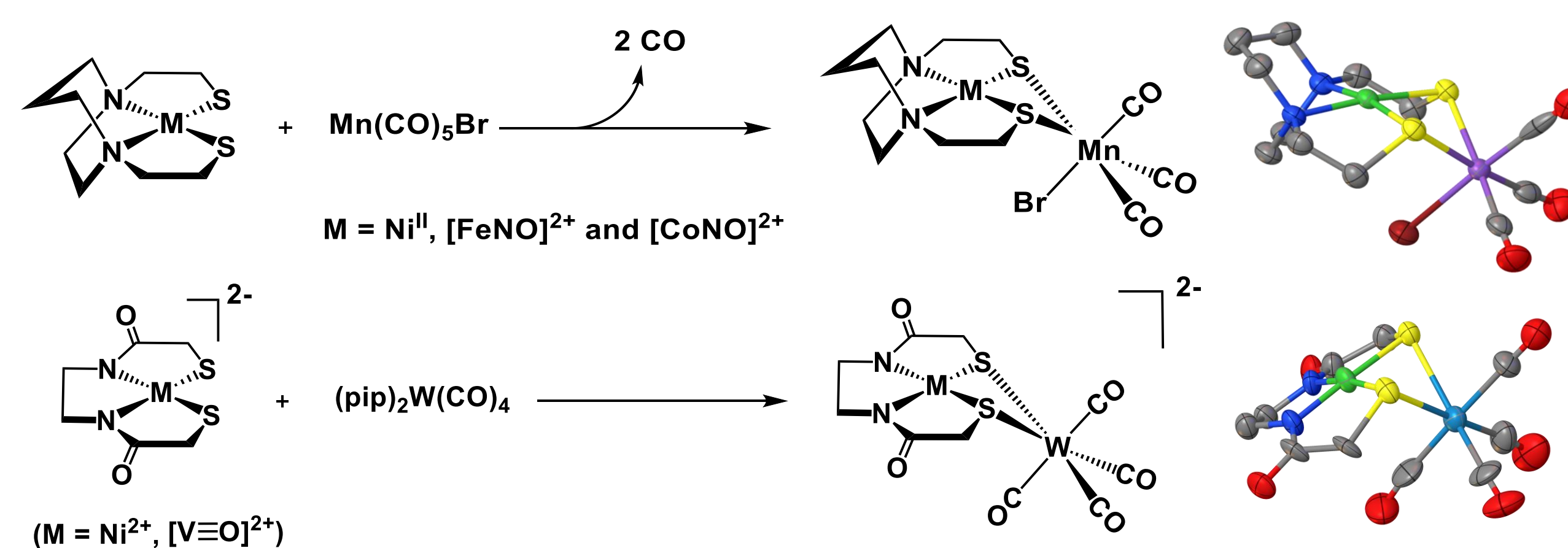
❖ Metal binding in metalloenzymes



❖ The *ema* (N,N'-ethylenebis(mercaptoacetamide)) ligand as Cys-X-Cys biomimetic (Holm, 1990's)

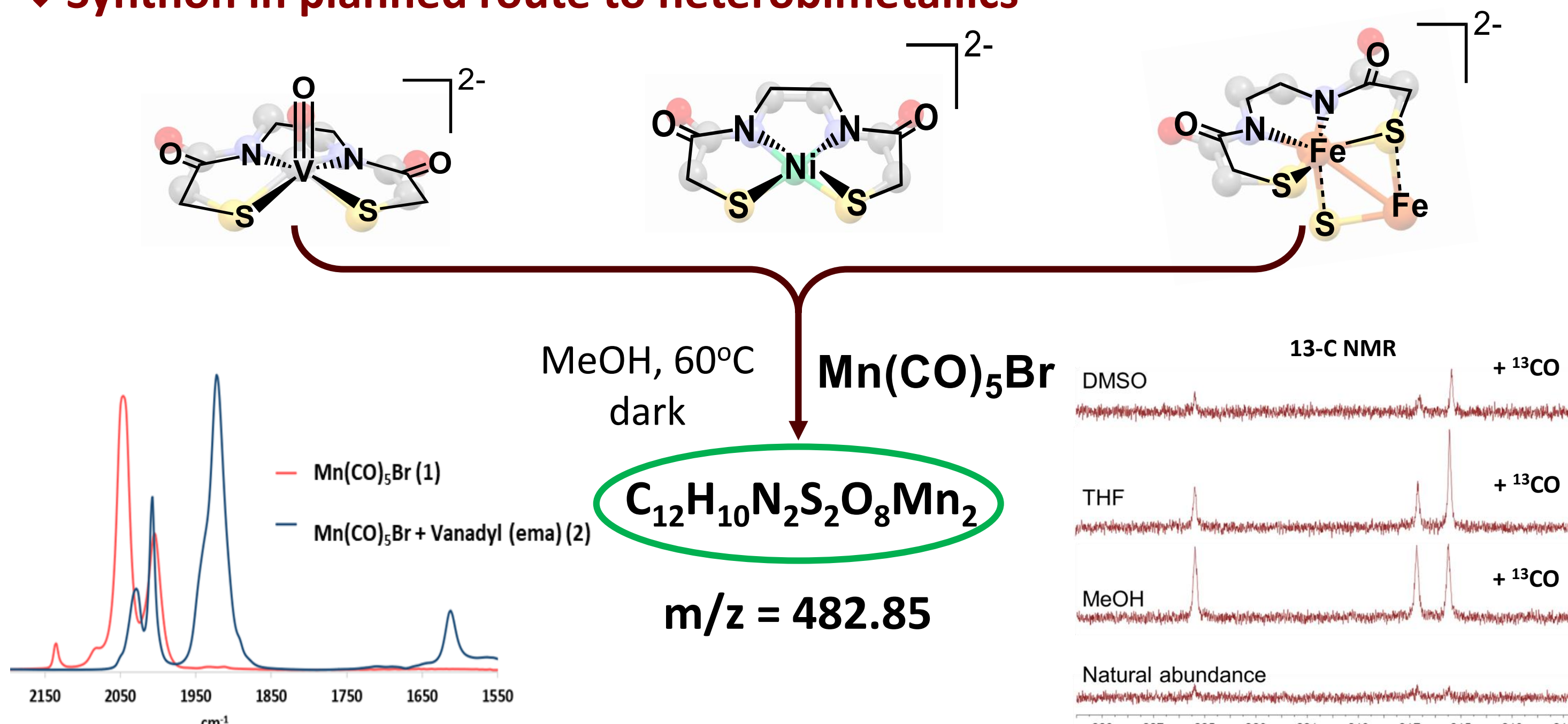


❖ Metallodithiolates as ligands for metal carbonyls yield heterobimetallics



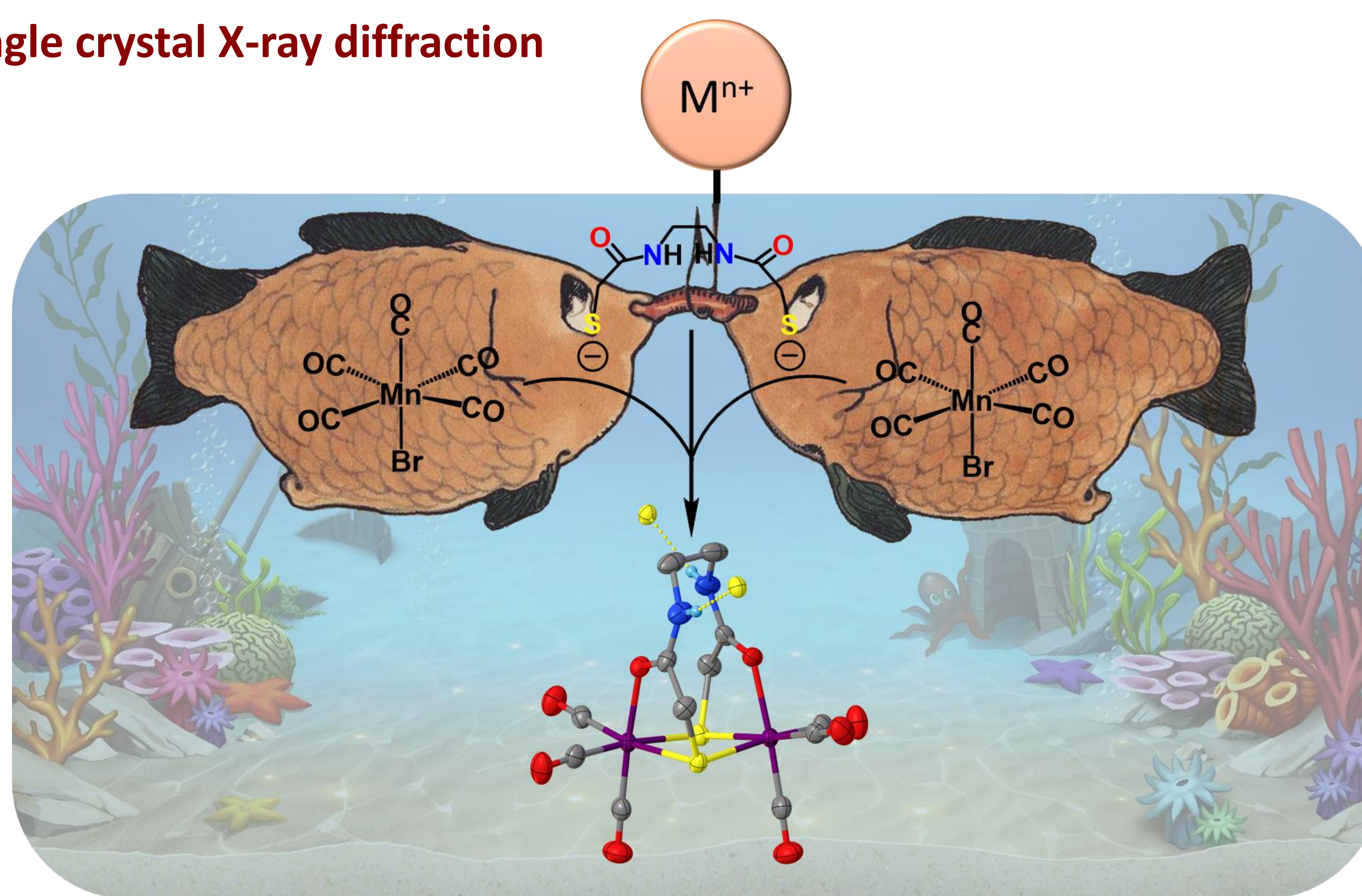
"The Observations"

❖ Synthon in planned route to heterobimetallics



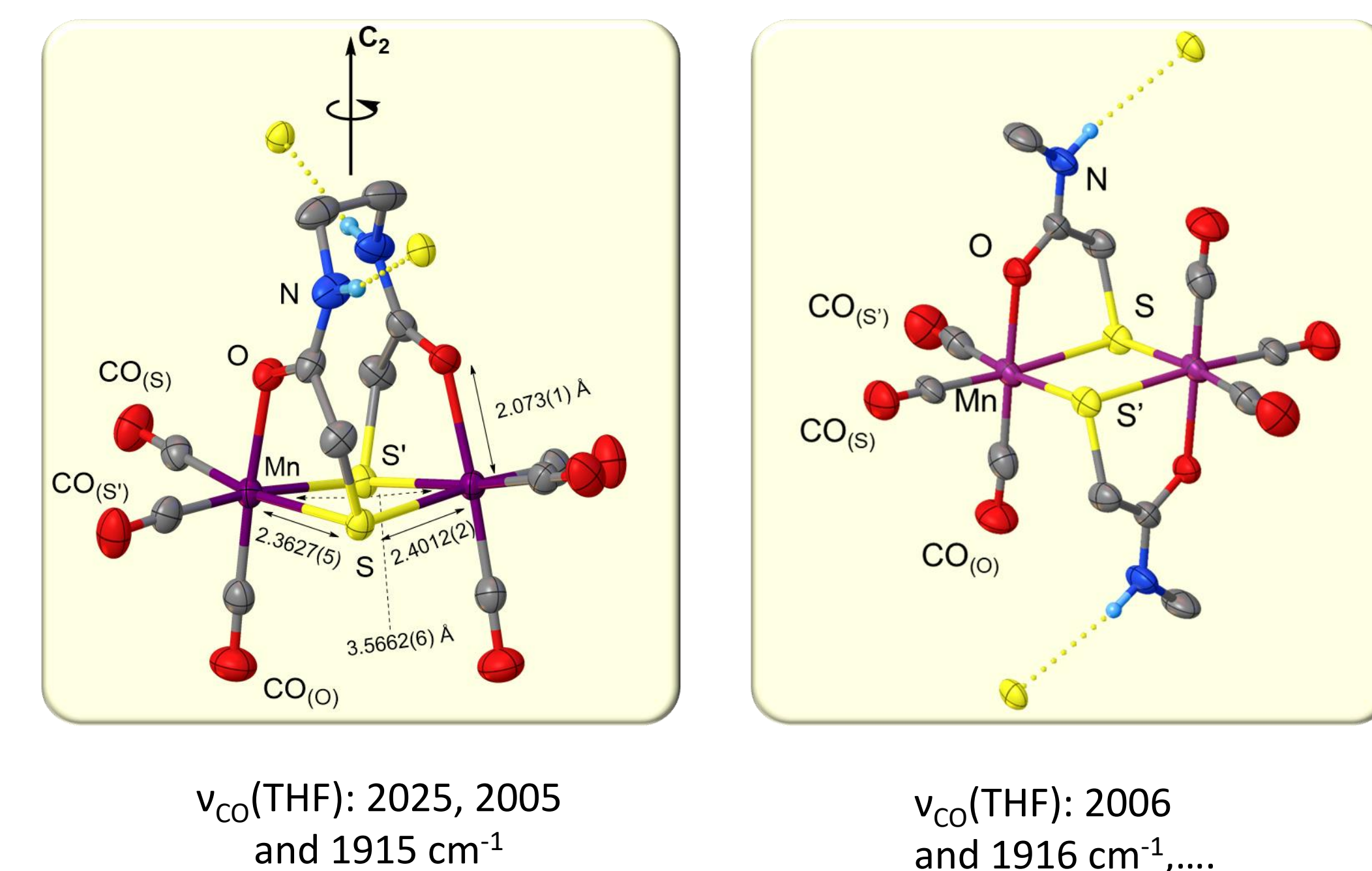
The "Two-manganese" Product

❖ Single crystal X-ray diffraction



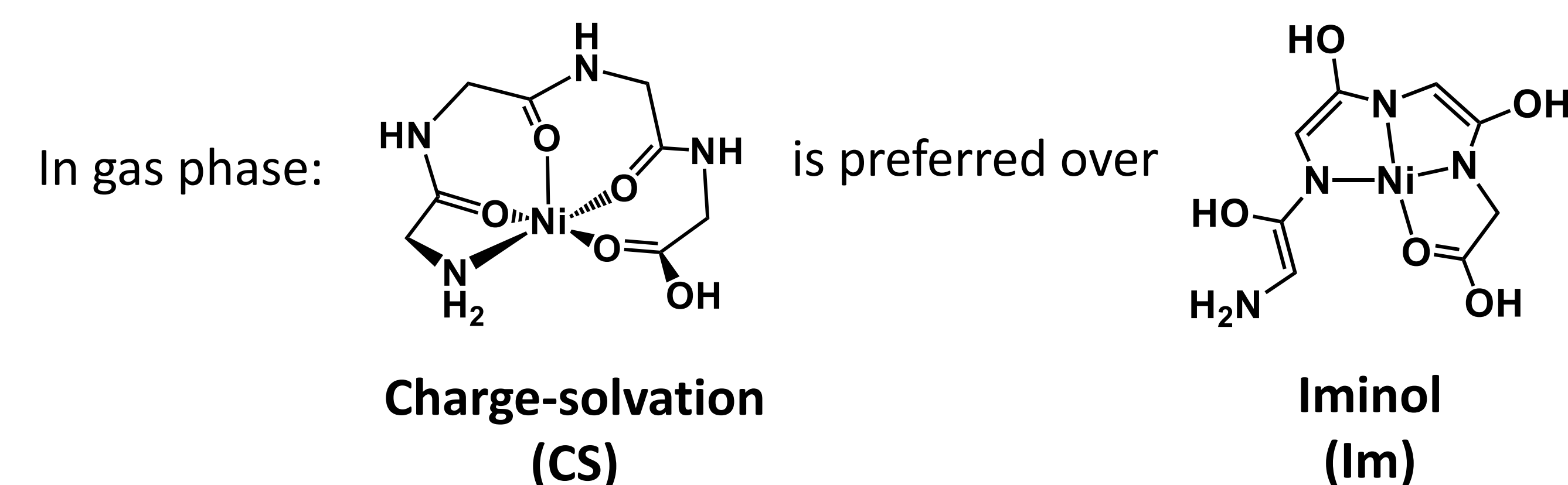
Graphic includes "Two Fishes, One Hook"; Paul Klee, 1901

XRD structures of tethered and non-tethered Mn₂

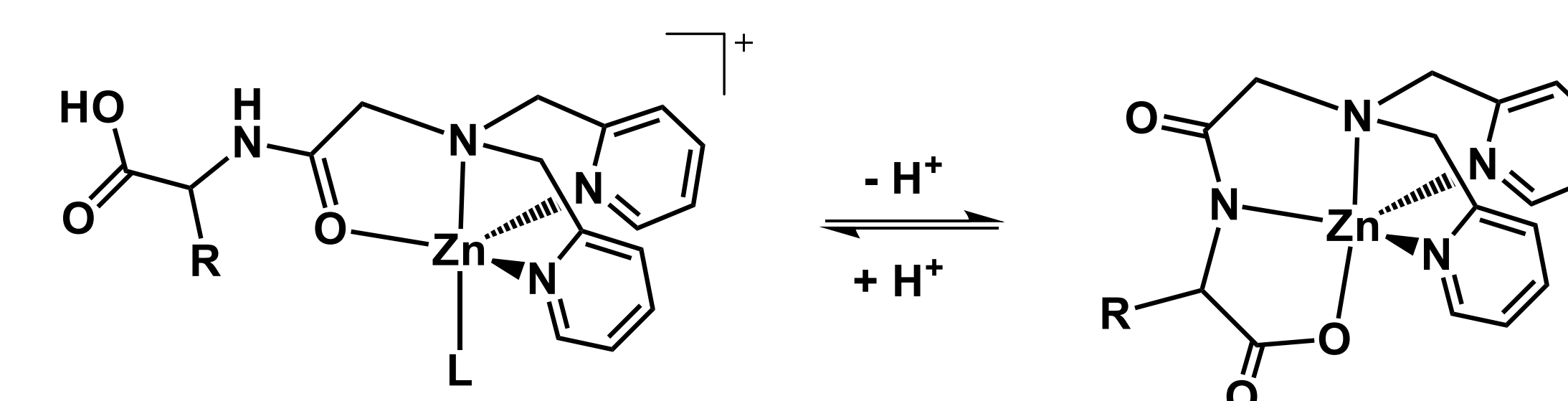


"The Conversation"

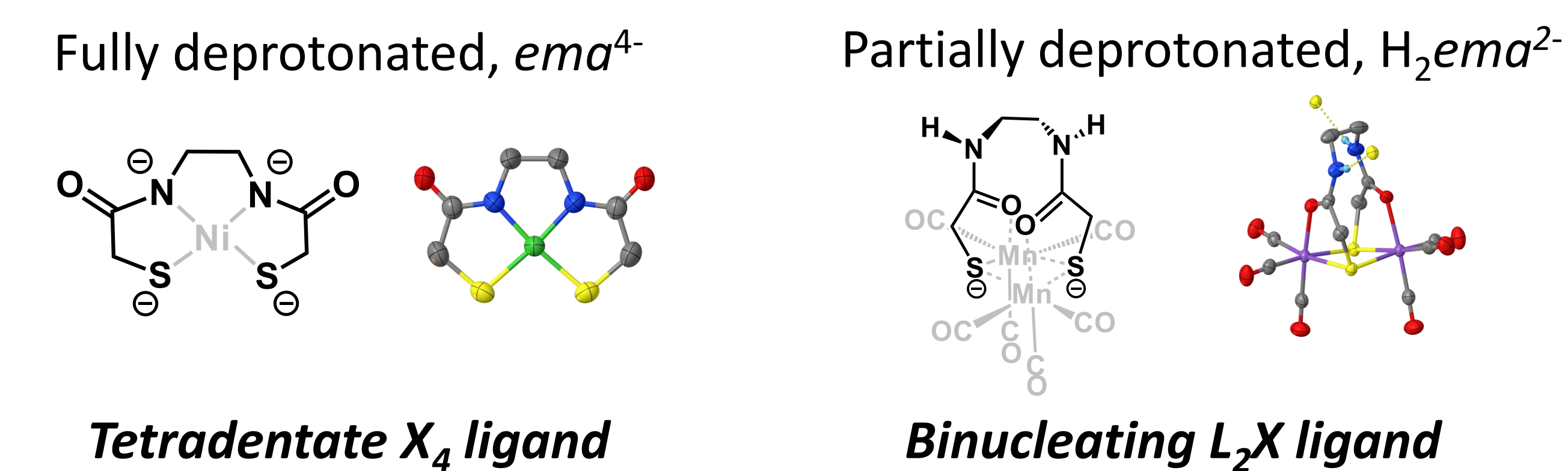
❖ "Tension" between carboxamide O and deprotonated N engaging in metal binding in small peptides described by Oomens *et al.*, *Phys.Chem.Chem.Phys.*, 2016.



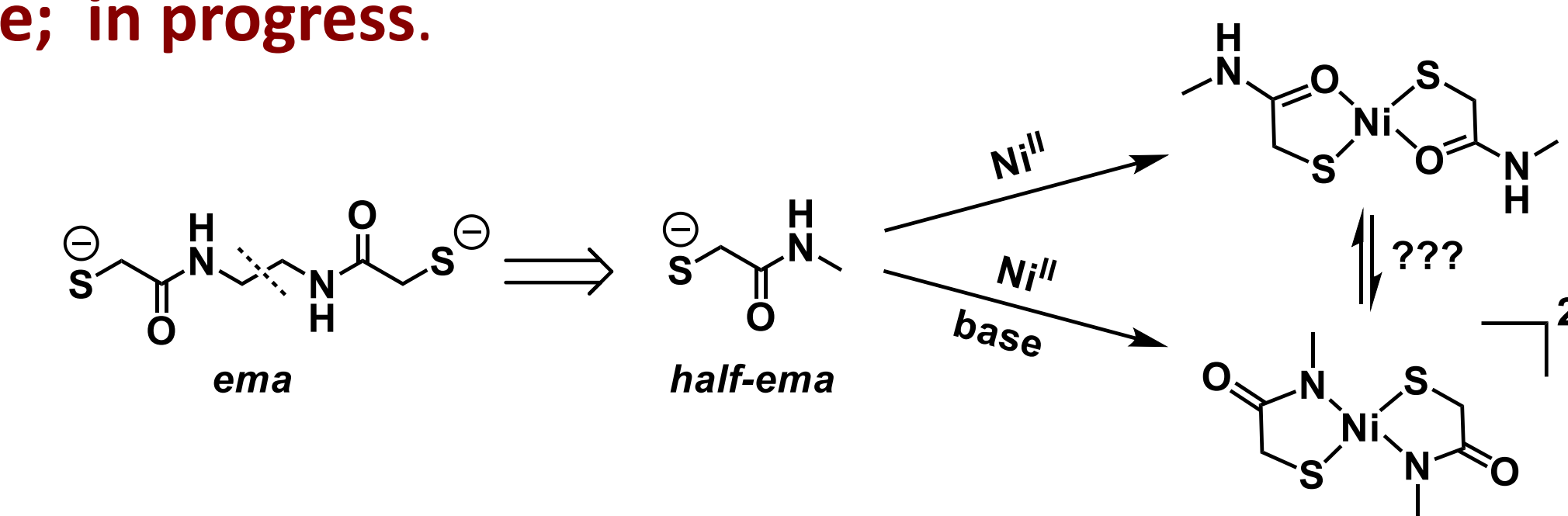
❖ Reversible binding mode switching in amino acid – tethered tripodal ligand observed by Alsfasser *et al.*, *Inorg. Chem.* 2005.



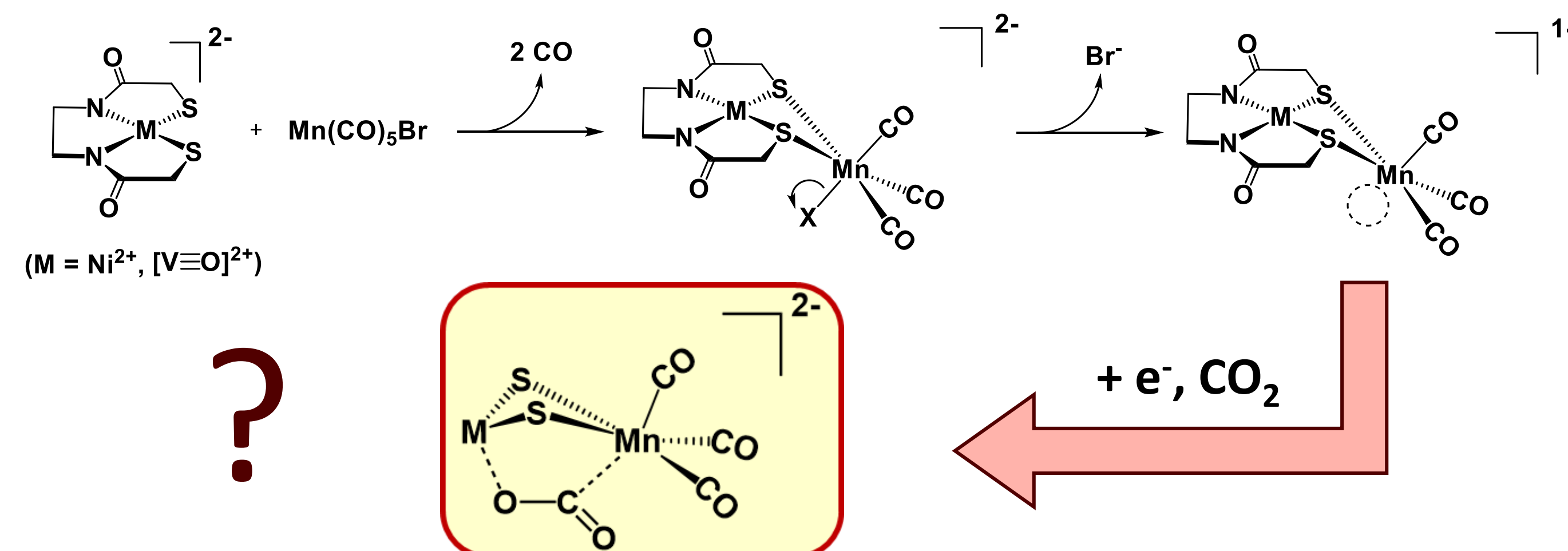
❖ Multiple metal-binding possibilities of the *ema* ligand, this work



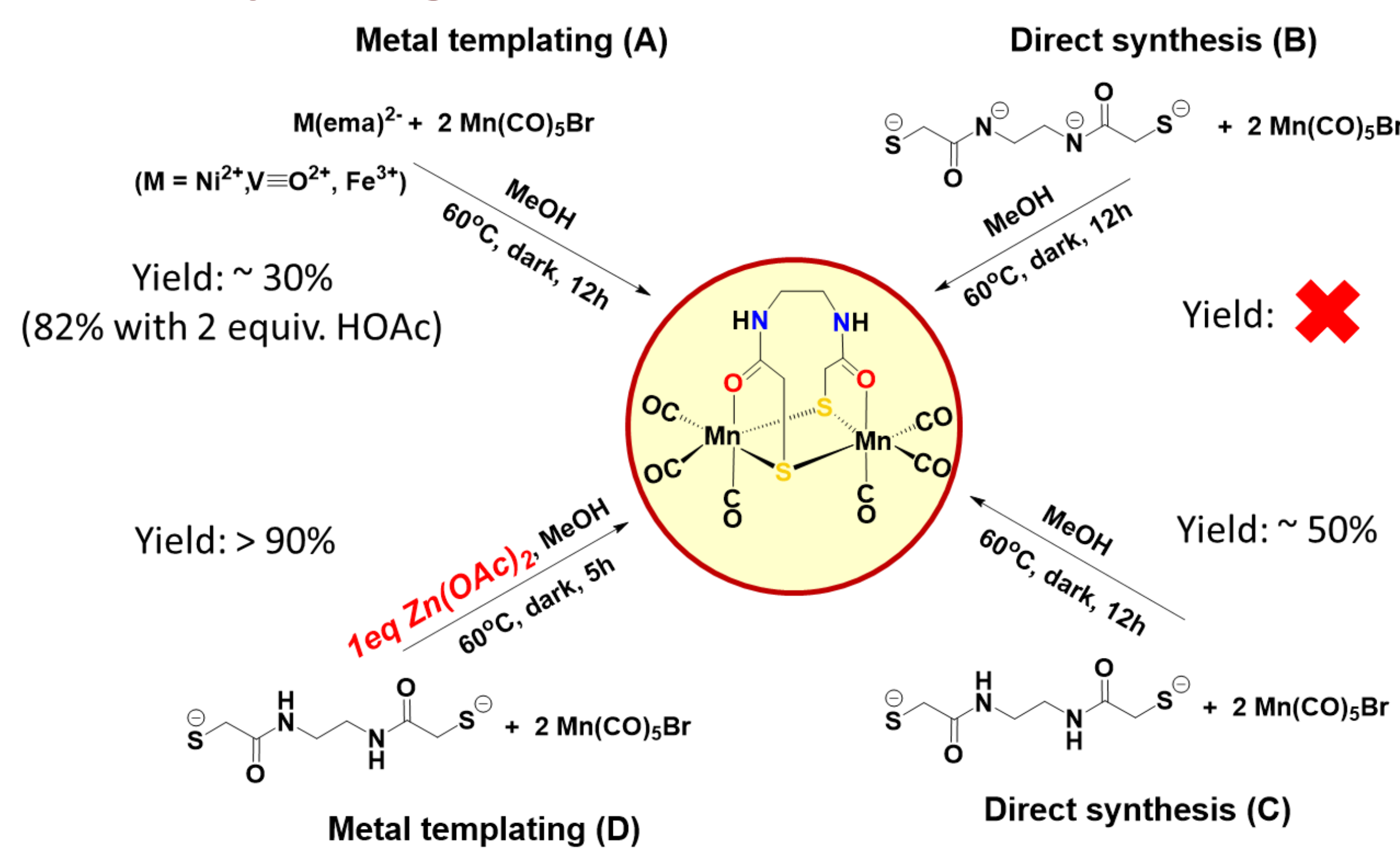
❖ Mercaptoacetamide-type ligand as model for Cys-containing small peptide; in progress.



"The Plan"



Metal-templating effect



References

- 1) a) *Science* **2002**, 298, 567 - 572; b) *Nature Structural Biology* **2003**, 10, 271 - 279; c) *PNAS* **2004**, 101, 446-451
- 2) *Acc. Chem. Res.* **1997**, 30, 123-130
- 3) *Inorg. Chem.* **1991**, 30, 734-742
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- 5) a) *Angew. Chem. Int. Ed.* **2005**, 44, 1217 - 1220; b) *Inorg. Chem.* **2014**, 53, 17, 9095-9105.
- 6) *Phys. Chem. Chem. Phys.* **2016**, 18, 26923-26932
- 7) *Inorg. Chem.* **2005**, 44, 4796-4805.