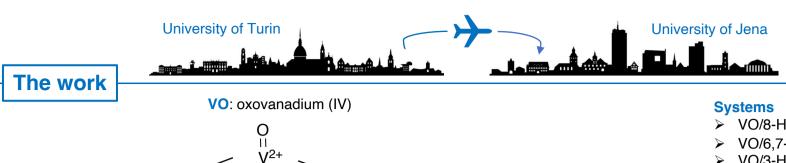
EPR charactherization of oxovanadium coordination complexes

Grantee name: Matteo Marafante - PhD Project: Thermodynamic study of first-row transition metal ions complexes of biomedical interest



3-HC: 3-hydroxycoumarin

6,7-DHC: 6,7-dihydroxycoumarin

8-HQA: 8-hydroxyguinoline-2-carboxylic acid

KA: Kojic acid

- VO/8-HQA
- VO/6.7-DHC
- VO/3-HC
- VO/8-HQA/KA
- VO/8-HQA/6,7-DHC

Conditions

2% EtOH Aqueous solution (u.p.) 0.2 mM < [M]-[L] < 1 mM

EPR aguired at ~ 88K

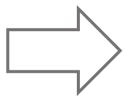
The approach

Potentiometry Previously done

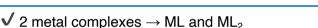




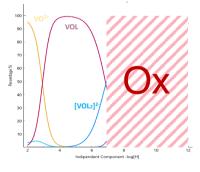
VO/8-HQA



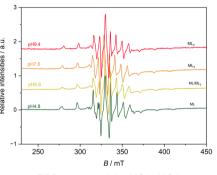
Speciation Model To be confirmed and refined



- ▲ VO signal lost due to oxidation above pH ~ 7.
- ✓ Free-O₂ experiments show the ML₂ presence up to pH 9.4
- PRefinement of the constants with further free-O2 pH experiments



↑ Speciation model obtained from experiments in the stability region



↑ EPR spectra of the VO/8-HQA 1:3 system at various pH

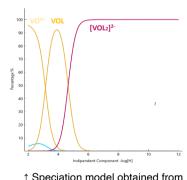
✓ 2 metal complexes

→ ML and ML₂

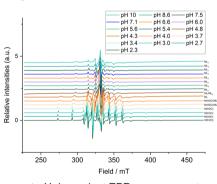
VO signal decrease at alkaline pH (oxidation)

✓ Free-O₂ Uv-vis experiments confirm oxidation

Speciation model and EPR agree



↑ Speciation model obtained from experiments in the stability region (valid in free-O2 enviroment)



VO/6,7-DHC

↑ pH dependent EPR measurement of the VO/6,7-DHC 1:3 system

Other systems

VO/3-HC No proof of coordination using any techniques (potentiometry, UV-vis spectroscopy and EPR)

VO/8-HQA/KA A mixed complex is formed around neutrality (stoichiometry 1:1:1)

VO/8-HQA/6,7-DHC – 6,7-DHC coordination prevails on the 8-HQA coordination: VO/6,7-DHC ML is formed in solution













