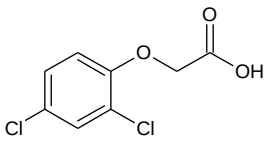
The geometry of Co(II), Ni(II) and Cu(II) complexes with chlorophenoxy herbicides determined by XAS and UV-Vis spectroscopies

Aleksandra Drzewiecka-Antonik[1], Anna Wolska[1], Paweł Rejmak[1], Marcin T. Klepka[1], Wiesława Ferenc[2]

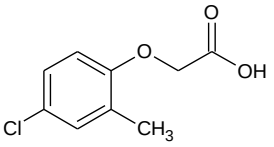
[1]Institute of Physics, Polish Academy of Sciences, Warsaw, Poland; [2]Faculty of Chemistry, Maria Curie-Skłodowska University, Lublin, Poland

Molecular structure



2,4-D

2,4 - dichlorophenoxyacetic acid



MCPA

4-chloro-2 methylphenoxyacetic acid

Introduction

- Chlorophenoxy herbicides persist about 1 month in soil and are highly soluble in water. Before they are degraded, they can react with elements present in soil and plant tissues;
- The uptake and translocation of metal ions as Co(II), Ni(II) and Cu(II) are observed via 2,4-D and MCPA herbicides;
- Usually the studies of such connection are focused on the physicochemical properties, not on the structure;
- Complexes rarely crystalize and crystallization can change the structure;
- XAFS and UV-Vis spectroscopies work for the compounds in any form!

Measurements

XAFS beamline at Elletra, Trieste, Italy

Elettra Sincrotrone Trieste

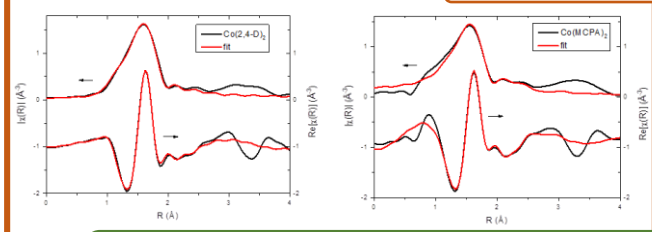
SHIMADZU **UV-VIS** Spectrophotometer UV-2600Plus (our lab)

Co(II) complexes with 2,4-D and MCPA

Ni(II) complexes with 2,4-D and MCPA

Cu(II) complexes with 2,4-D and MCPA

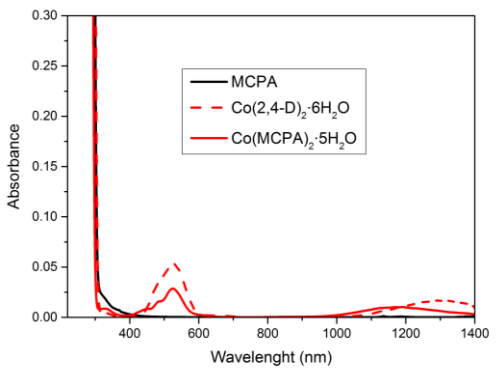
Moduli and a real part of the FT EXAFS oscillations with the best fit



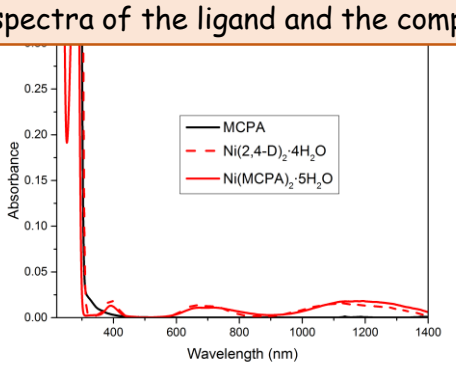
Six O atoms were found above 2 Å & two C atoms around 3 Å from Co(II)/Ni(II) cations

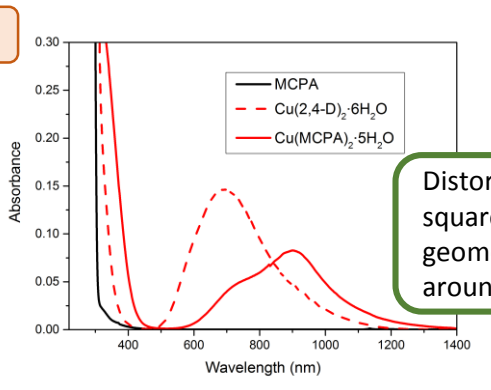
Four O atoms below 2 Å & two or four C atoms were found for Cu(II) with 2,4-D and MCPA, respectively

Solid state UV-Vis spectra of the ligand and the complexes



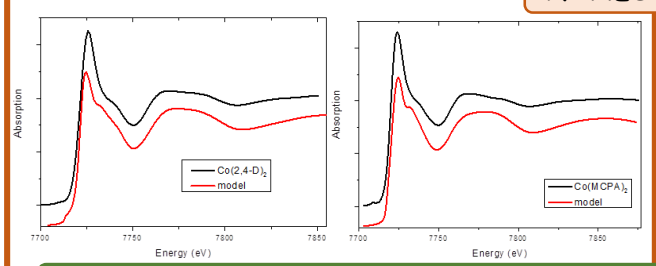
Octahedral geometry around Co/Ni at +2 oxidation state





Distorted square planar geometry around Cu^{+2}

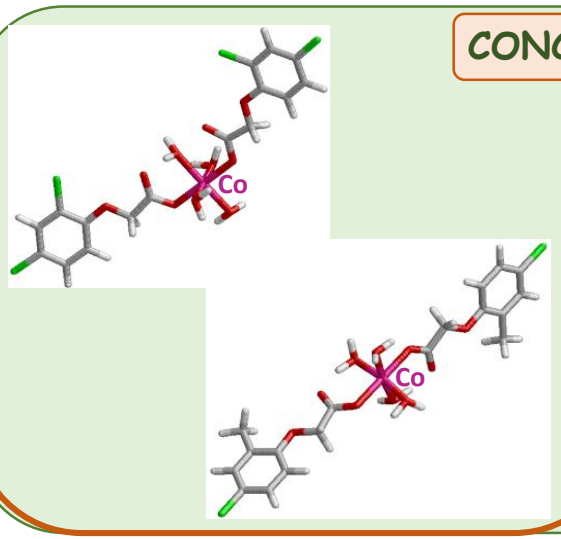
XANES spectra for optimized the models vs. experimental data

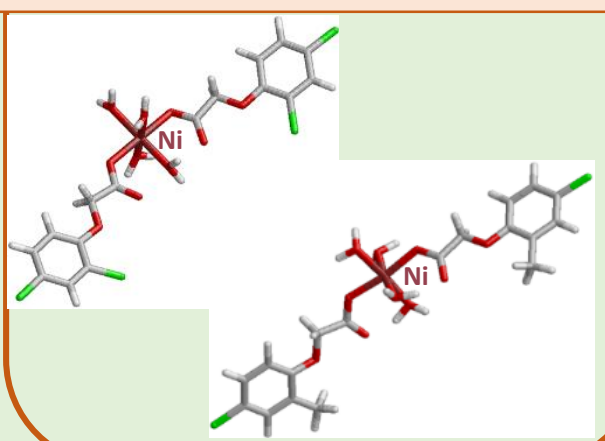


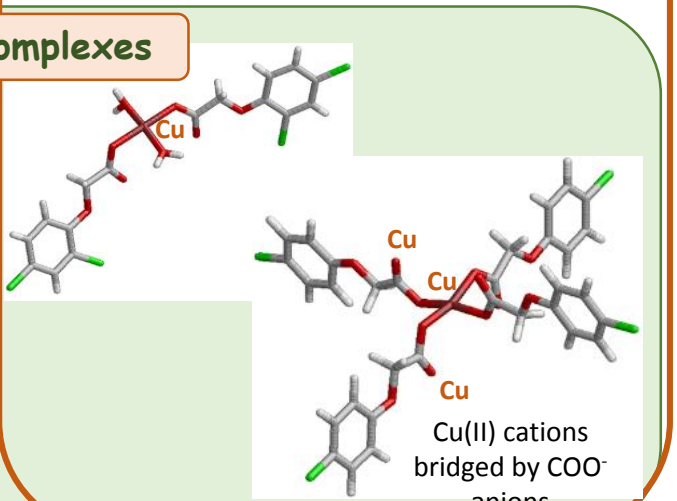
Two monodentate herbicide anions and four or two water molecules coordinate to the metal cations

Two coordination modes of the ligands

CONCLUSION: Molecular structure of the complexes







Cu(II) cations bridged by COO^- anions