

## Mn(II) complexes with 2,4-D and MCPA herbicides: IR and XAFS studies

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Manganese is one of the essential elements for plants, playing several crucial roles in their growth and development. Plants primarily absorb manganese in its ionic form, specifically as Mn(II). This divalent manganese, present in soil and plant tissues, may interact with anions as phenoxyacetate herbicides, forming metal-organic complexes. In 2017, the uptake and transfer of metal ions such as Mn(II) by 2,4-D and MCPA was documented<sup>1</sup>. Therefore, it has become important to study the structure and biological properties of such connections.

In order to get structural information about such compounds, we have synthesized analogous complexes in laboratory conditions<sup>2</sup>. The synthesis gave rise to the formation of hydrated complexes. The fluorescence X-ray analysis as well as elemental and thermal analyses allowed to determine the composition of complexes, namely Mn(2,4-D)<sub>2</sub>·2H<sub>2</sub>O and Mn(MCPA)<sub>2</sub>·2H<sub>2</sub>O. The infrared spectra of herbicides and their Mn(II) complexes contain several diagnostic bands that can point out the functional group of herbicide molecules interacting with metal cation<sup>2</sup>. A doublet structure of absorption band corresponding to a carboxyl C=O stretching vibration is observed for acid molecules of herbicides. This band is not observed for Mn(II) complexes, indicating acid deprotonation and stretching bands of deprotonated carboxyl groups are observed on the IR spectra of the complexes. Moreover, the positions of bands, assigned to the C-Oether and C-Cl stretching vibrations suggest that neither O ether nor Cl atoms from herbicide molecules are coordinated to the Mn(II).

The XAFS measurements for the complexes with 2,4-D and MCPA herbicides were performed at ELETTRA synchrotron (Trieste, Italy). The EXAFS analysis (Fig.1) revealed that the complexes forms a polymeric structure with six O atoms bonded to Mn(II) ion. The O atoms originate from four carboxylate groups of herbicide molecules and two H<sub>2</sub>O solvent molecules. The number of carboxylate groups confirmed the presence of four C atoms in the second coordination sphere of Mn(II). The proposed polymeric models of manganese complexes were refined by DFT calculations and verified by XANES.

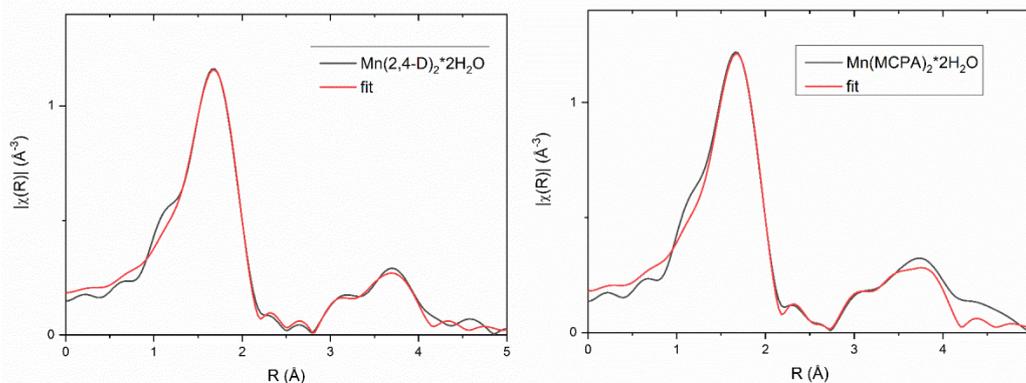


Figure 1. EXAFS fitting of the experimental oscillations (black line) and the fitting result (red line).

### References

1. E. Skiba, J. Kobyłecka, W.M. Wolf, Environ. Pollut. 220 (2017) 882.
2. A. Drzewiecka-Antonik, W. Ferenc, B. Mirosław, D. Osypiuk, J. Sarzyński, Polyhedron 207 (2021) 115370.