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Complexation of malic acid with cadmium(II) probed by electrospray ionization mass spectrometry

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ABSTRACT

Electrospray ionization was used as a technique for the characterization of the interactions between cadmium(II) ions and malic acid (**1**) in aqueous solution. Particular attention was paid to the nature of the species formed, which generally correspond to complexes of CdX^+ cations with neutral malic acid, where X either is the counterion of the metal salt used as a precursor (i.e. X = Cl, I) or corresponds to singly deprotonated malic acid. In pure water solutions, also highly coordinated complexes $[Cd(\mathbf{1}\text{-H})(\mathbf{1})_2]^+$ and $[CdCl(\mathbf{1})_2]^+$ were detected, whereas the most abundant complexes detected in a sample of soil solution were: $[Cd(\mathbf{1}\text{-H})(\mathbf{1})]^+$ and $[CdCl(\mathbf{1})]^+$. With respect to possible application in environmental analysis, the effects of (i) metal salts present in solution, (ii) modest mineralization, and (iii) the matrices of real soil solutions were probed. While the presence of other metals leads to additional complexes, the characteristic species containing both cadmium(II) and malic acid can still be detected with good sensitivity.

1. Introduction

Among important components of soil matrices twinning (hazardous) metals are low molecular weight organic acids (LMWOAs) [1,2]. LMWOAs form more or less stable complexes playing important roles in the uptake of metals by plants [3]. Malic acid (2-hydroxybutanedioic acid, compound **1**) occurs in fruits and other plant parts and is among the most abundant LMWOAs (with oxalic, citric, tartaric and acetic acid) in soils and soil solutions [2]. As a multiple heteroatom-functionalized molecule, malic acid can be expected to act as a ligand towards metal ions present in aqueous solutions [4]. Our specific interest in this respect concerns the relevance of coordination complexes between metal ions and LMWOAs for the migration behavior of metal ions in soils and their transport properties in the passage through plant membranes. For this reason, we search for methods for the investigation of the interactions between LMWOAs and metal ions, with a particular focus on environmentally problematic metals.

Two central problems with respect to the detection of such interactions are the organic matrix present in real environmental samples as well as the low concentrations to be expected for both the LMWOAs and the metal species. The organic matrix itself does not prevent the direct detection of the cadmium/LMWOAs species, when very sensitive electrochemical methods [5,6], especially stripping voltammetry [7,8], are used. Nevertheless, the selectivity of these methods is limited compared to others and both the accurate description of the species stoichiometry and the assignment of a specific molecular structure are not at all trivial [9]. Further, otherwise extremely powerful and highly selective methods including chromatographic separation may not allow the detection of metal species because of the changes in speciation upon addition of a mobile phase, adsorption effects, etc. Specifically, the conventional workup for the detection of LMWOAs with typical sample pretreatment via chromatographic [10–12] or electrophoretic [13] separations is likely to destroy any cadmium/malic acid complexes eventually present in the untreated samples and/or it may cause changes in the speciation of both the metal and the LMWOAs [14–16]. As an alternative, metal complexes with organic ligands in real environmental samples can be detected via a direct mass spectrometric assay. This method is based upon electrospray ionization mass spectrometry (ESI-MS) and does not involve any prior workup of the samples [17–19]. We have recently used these techniques for the speciation analysis of metal ions interacting with fungicides [20,21].

The main aim of the present study was to investigate Cd-malic acid interactions using ESI-MS. Additionally, the impacts of potassium chloride, of modest mineralization, and of a real soil solution

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Table 1
pH value and content of selected elements in the soil solution prepared 3-times.

	pH	Al (mg L^{-1})	Fe (mg L^{-1})	K (mg L^{-1})	Ca (mg L^{-1})	Mg (mg L^{-1})	As (μg L^{-1})	Cd (μg L^{-1})	Cr (μg L^{-1})	Cu (μg L^{-1})	Mn (μg L^{-1})	Ni (μg L^{-1})	Pb (μg L^{-1})	Zn (μg L^{-1})
Mean	5.03	14.7	2.89	8.13	4.76	2.64	39.7	3.17	18.9	13.4	21.0	3.69	66.4	51.5
SD	0.04	0.4	0.45	0.18	0.14	0.03	1.7	0.12	0.2	0.4	0.1	0.23	3.6	1.1

SD: standard deviation.

Table 2
Mean annual pH value and content of selected elements in the tap water used [27].

	pH	Ca (mg L^{-1})	Mg (mg L^{-1})	Na (mg L^{-1})	Al (μg L^{-1})	Fe (μg L^{-1})	As (μg L^{-1})	Cd (μg L^{-1})	Cr (μg L^{-1})	Cu (μg L^{-1})	Mn (μg L^{-1})	Ni (μg L^{-1})	Pb (μg L^{-1})
Mean	7.60	44.7	7.34	11.5	19.8	78.3	0.408	0.0833	0.508	4.33	4.08	1.25	0.575
SD	0.05	9.4	0.29	0.3	3.3	11.4	0.132	0.0312	0.028	1.43	1.11	0.30	0.169

SD: standard deviation.