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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.

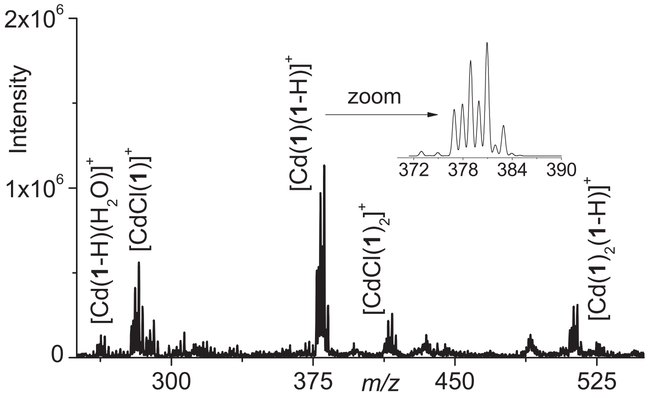

Fig. 1. Positive mode ESI mass spectrum in the range m/z 250–550 of a mixture of malic acid (**1**, 5×10^{-3} mol L^{-1}) and CdCl$_2$ (5×10^{-4} mol L^{-1}) in water, pH 3.5. As an example, the inset near the most abundant species shows the isotope pattern of the [Cd(**1**–H)(**1**)]$^+$ complex on an expanded mass scale.

as co-solvent on the formation and detection of Cd-malic acid species were studied. The results may contribute to a better understanding of Cd uptake by metals accumulating plants, and the knowledge of the composition and stoichiometry of the Cd-malic acid species may help to assess the transport of the species involved through the plant plasma membrane.

2. Experimental

The experiments were performed with a Finnigan LCQ Advantage ion-trap mass spectrometer (ThermoFinnigan, San Jose, CA, USA) fitted with an electrospray ionization source operated in positive and negative-ion mode [22]. Diluted solutions of malic acid and appropriate Cd(II) salts in pure water were introduced into the ESI source via a fused-silica capillary at a flow rate of 0.7 mL h^{-1}. Nitrogen was used as the nebulizer gas. The operating conditions were set as follows: spray voltage 5.0 kV, capillary voltage 12 V, tube lens offset 47 V, heated capillary temperature 230 °C, sheath gas flow rate and auxiliary gas flow rate 20–30 arbitrary units. Mass spectra were recorded from m/z 50 to 2000. Collision-induced dissociation (CID) of mass-selected precursor ions was achieved by RF-excitation of the ions within the He buffer gas present in the ion trap as the collision partner. The collision energy was optimized for each experiment and is expressed in terms of the manufacturer's normalized collision energy (%), where the range from 0 to 100% corresponds to a resonance excitation *a.c.* signal of 0–2.5 V (zero-to-peak) at the secular frequency of the ion of interest. The actual collision energies depend on the m/z values of the parent ions, but conversion to an absolute energy scale is feasible via an empirical calibration [23] via the loss of pyridine from mass-selected (2,5-dimethylbenzyl)pyridinium ion, which leads to the phenomenological conversion E_{coll} (kJ mol^{-1}) = (7.3 ± 0.3)·E_{coll} (%) for the present experiments [24].

Standard solutions were prepared from CdCl$_2$ or CdI$_2$ salts (purum), racemic malic acid (HPLC grade), both Sigma Aldrich (Czech Republic), and ultrapure water (>18 MΩ). Stock solutions were 10^{-3} mol L^{-1} in CdCl$_2$ (CdI$_2$) and 10^{-2} mol L^{-1} in malic acid, then diluted to the desired concentrations.

The soil solution (Table 1) was prepared by over-night water extraction of an untreated, fresh soil sample with a 1:10 (w/w) ratio of soil and ultrapure water, and subsequent centrifugation (100 RCF) and filtration using a 0.2 μm syringe filter (Whatman, Schleicher and Schuell). The soil sample came from the experimental plantation of speckled alder on formerly clear-felled area in the Jizerské Hory Mts., Northern Bohemia, Czech Republic [25,26]. The composition of the tap water used is given in Table 2.

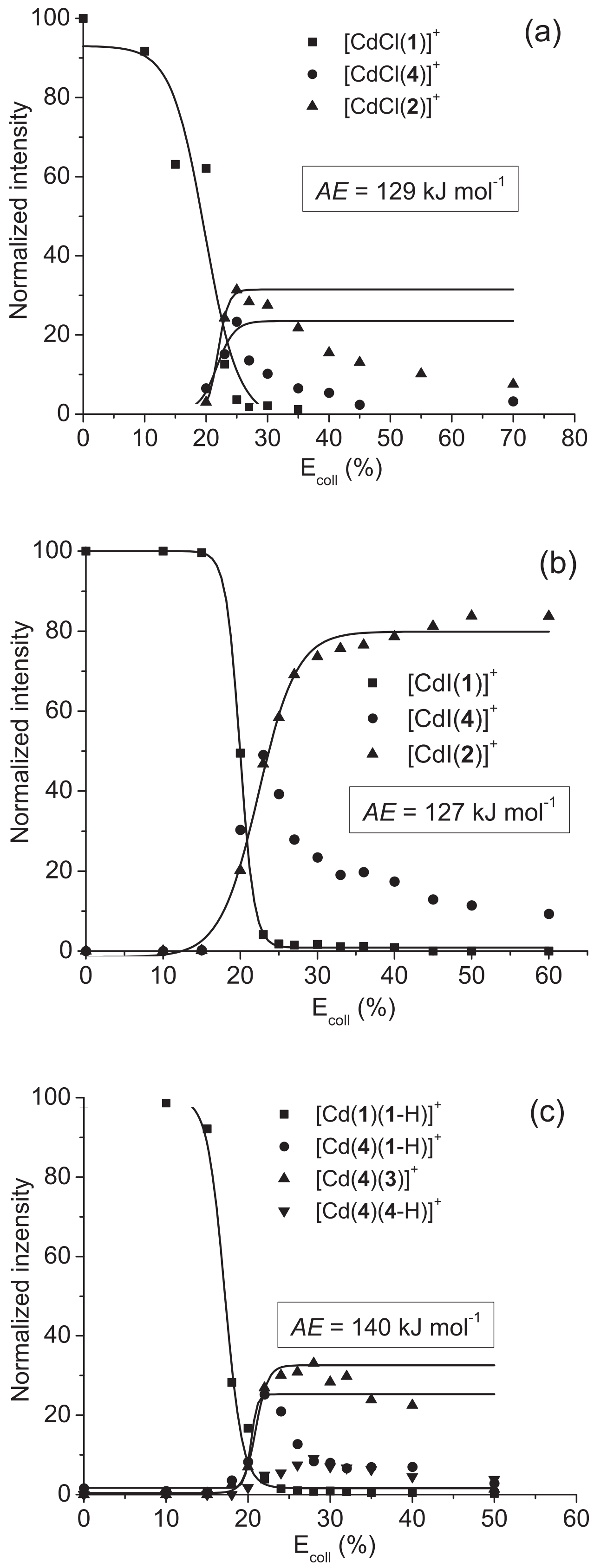

Fig. 2. Energy-dependence of fragment ion abundances for (a) [CdCl(**1**)]$^+$, (b) [CdI(**1**)]$^+$, and (c) [Cd(**1**)(**1**-H)] derived from independent CID experiments with the mass-selected ions. **1** stands for malic acid, **2** for $C_3H_4O_3$ (which can be assigned to e.g. pyruvic acid), **3** for lactic acid, and **4** for fumaric/maleic acid. *AE* stands for the appearance energy of the fragmentations.

3. Results and discussion

Fig. 1 shows a positive mode ESI mass spectrum of a diluted mixture of malic acid (**1**) and $CdCl_2$ in water obtained under soft ionization conditions, in which the formation of multiply ligated species prevail [28–30]. The major ions observed can be divided into two groups; note that all listed *m*/*z* values refer to the isotopes (^{1}H, ^{12}C, ^{16}O, ^{35}Cl, ^{110}Cd, and ^{127}I). (i) Several Cd(II) complexes include the chloride counter ion originating from the precursor metal salt, e.g. $[CdCl(\mathbf{1})]^+$ (*m*/*z* 279) and $[CdCl(\mathbf{1})_2]^+$ (*m*/*z* 413). (ii) Other complexes consist of Cd(II) and deprotonated malic acid, $[\mathbf{1}\text{-H}]^-$, as anionic ligand, e.g. $[Cd(\mathbf{1}\text{-H})]^+$ (*m*/*z* 243), the corresponding water adduct $[Cd(\mathbf{1}\text{-H})(H_2O)]^+$ (*m*/*z* 261), the most abundant species $[Cd(\mathbf{1}\text{-H})(\mathbf{1})]^+$ (*m*/*z* 377), and the higher-order complex $[Cd(\mathbf{1}\text{-H})(\mathbf{1})_2]^+$ (*m*/*z* 511). The ratios of the various ions depend on the ionization conditions as well as the ratio of Cd(II) versus malic acid. In the following, we focus on the type of the species observed, rather than their relative abundances. In this context, we also explicitly note that the abundances of the ions observed in ESI mass spectra do not correlate with the situation in solution in a 1:1 fashion, but show more complicated dependences which are not addressed in this work [31–35].

The stoichiometry of the complex in exact mass 278.80 is not evident, it can be explained either by the chloro complex $[CdCl(\mathbf{1})]^+$ (exact mass 278.89) or by the formula $[Cd(\mathbf{1}\text{-H})(H_2O)_2]^+$ (exact mass 278.94). Collision-induced dissociation (CID) experiments aimed to probe which of the two complexes belongs to the mass 278.80 (Fig. 2a) were inconclusive, however, because the observed loss of water may arise from malic acid as well as from coordinated water. Likewise, a modeling of the measured isotope pattern could not fully exclude the presence of water complexes. To further characterize the complex structure, experiments with CdI_2 instead of $CdCl_2$ were designed (Fig. 3). The absence of the complex with mass 278.80 in spectrum obtained from CdI_2 mixture (Fig. 3) proved its origin from $CdCl_2$. Moreover, a $[CdI(\mathbf{1})]^+$ ion (exact mass 370.93) was observed which corresponds to the expected analogue to $[CdCl(\mathbf{1})]^+$ with iodine as a counterion.

Both $[CdX(\mathbf{1})]^+$ ions (X = Cl, I) were probed by CID experiments (Fig. 2a and b). The fragmentation patterns are similar and show a loss of H_2O from the malic acid ligand and a transformation of malic acid into a compound with the sum formula $C_3H_4O_3$ (**2**), that is a loss of neutral "CH_2O_2", either formic acid or $CO + H_2O$, which can be explained by a degradation of malic acid to, for example, pyruvic acid (2-oxopropanoic acid) complexed as a ligand to the metal center (Fig. 4). The fragmentation threshold expressed as the phenomenological appearance energies is slightly higher for $[CdCl(\mathbf{1})]^+$ (146 kJ mol^{-1}) compared to $[CdI(\mathbf{1})]^+$ (127 kJ mol^{-1}).

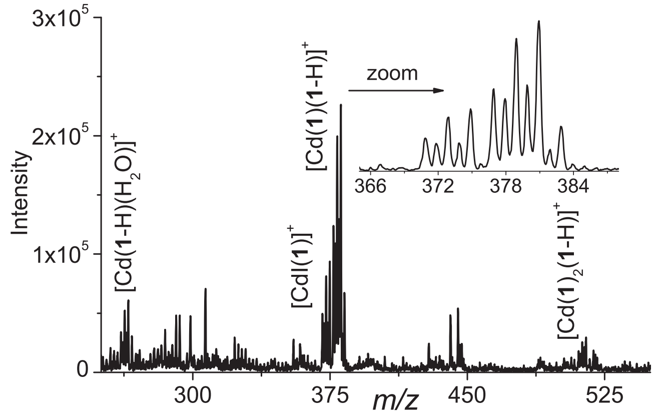

Fig. 3. Positive mode ESI mass spectrum in the range *m*/*z* 250–550 of a mixture of malic acid (**1**, 5×10^{-4} mol L^{-1}) and CdI_2 (5×10^{-5} mol L^{-1}) in water, pH 6. As an example, the inset near the most abundant species shows the isotope patterns of the $[Cd(\mathbf{1}\text{–H})(\mathbf{1})]^+$ and $[CdI(\mathbf{1})]^+$ complexes on an expanded mass scale.

The fragmentation of the most abundant complex $[Cd(\mathbf{1}\text{-H})(\mathbf{1})]^+$ (*m*/*z* 377) present in both Cd solutions (Fig. 2c) shows an initial loss of H_2O followed by expulsion of another water molecule or a competing decarboxylation (loss of CO_2), where the latter putatively transforms malic acid into lactic acid (2-hydroxypropanoic acid, **3**), see Fig. 4. The fragmentation threshold is slightly larger for $[Cd(\mathbf{1}\text{–H})(\mathbf{1})]^+$ (140 kJ mol^{-1}) than for $[CdI(\mathbf{1})]^+$ and similar to that of $[CdCl(\mathbf{1})]^+$.

In order to assess the effect of the presence of other metal cations on the cadmium-malic acid species, the experiments with $CdCl_2$ and malic acid were repeated after addition of KCl (10^{-6} mol L^{-1}); note that all listed *m*/*z* values refer to ^{39}K. The presence of K^+ in the solution is reflected by the formation of $[K(\mathbf{1})_2]^+$ (*m*/*z* 308) in Fig. 5. Potassium is also incorporated into the $[CdCl(\mathbf{1})_2]^+$ cation

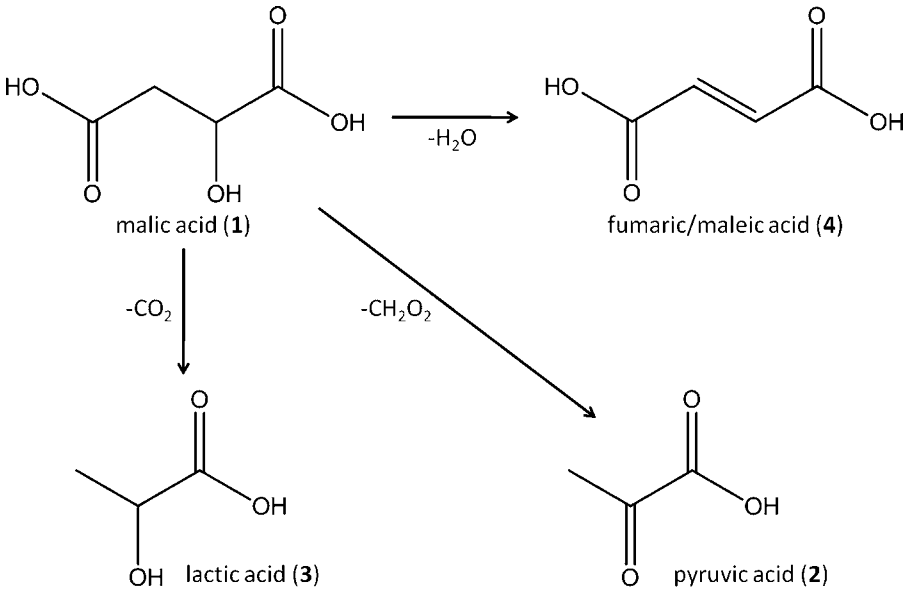

Fig. 4. Proposed degradation pathways of malic acid under ESI conditions. Note that these degradations may not at all take place in solution, but may rather result from the mass spectrometric sampling.

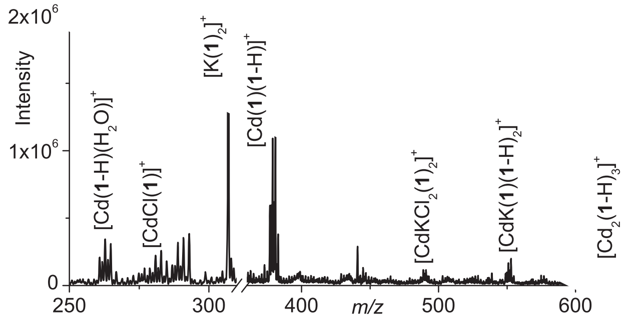

Fig. 5. Positive mode ESI mass spectrum in the range *m/z* 250–650 of a mixture of malic acid (**1**, 5×10^{-4} mol L^{-1}) and $CdCl_2$ (5×10^{-5} mol L^{-1}) in water in the presence of KCl (10^{-6} mol L^{-1}), pH 6.

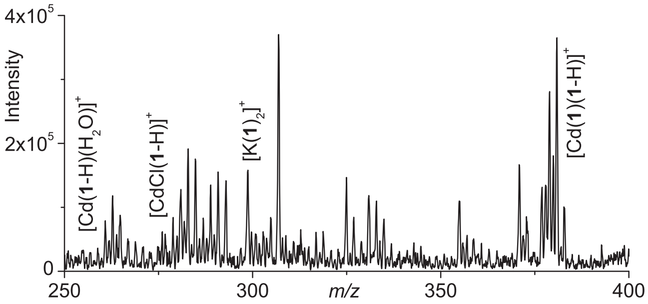

Fig. 6. Positive mode ESI mass spectrum in the range *m/z* 250–400 of malic acid (**1**, 2.5×10^{-4} mol L^{-1}) and $CdCl_2$ (2.5×10^{-5} mol L^{-1}) using a mixture of water/tap water (1:1), pH 6.

(*m/z* 413) to afford the ion-pair complex $[CdKCl_2(\mathbf{1})_2]^+$ (*m/z* 487). The species $[CdK(\mathbf{1})(\mathbf{1}\text{-H})_2]^+$ (*m/z* 549) can be conjugated from neutral $[CdCl_2(\mathbf{1})_2]$ and $[K(\mathbf{1})_2]^+$ via loss of two HCl molecules. Last but not least, the presence of KCl increases the over ion abundances by almost one order of magnitude, which can be ascribed to the increase of solution conductivity [36].

Likewise, the impact of a modest mineralization was probed by preparing a solution of malic acid (2.5×10^{-4} mol L^{-1}) and $CdCl_2$ (2.5×10^{-5} mol L^{-1}) in a mixture of ultrapure water and tap water (Table 2) (1:1) as a solvent (Fig. 6). The most intensive species there are $[Cd(\mathbf{1}\text{-H})(\mathbf{1})]^+$ (*m/z* 377) and $[K(\mathbf{1})_2]^+$ (*m/z* 308) with the ion abundances being on about one order of magnitude lower than in pure water solution of 10^{-6} mol L^{-1} KCl.

Likewise, a representative soil solution from the forest experiment with alder plantation [25,26] was used to probe possible matrix effects (Fig. 7). In addition to the most abundant complexes between cadmium and malic acid, e.g. $[Cd(\mathbf{1}\text{-H})(\mathbf{1})]^+$ (*m/z* 377), a signal due to $[Na(\mathbf{1})]^+$ (*m/z* 157) is observed which is ascribed to sodium present in the soil solution. The absolute intensity of the most abundant species $[Cd(\mathbf{1}\text{-H})(\mathbf{1})]^+$ is comparable with that obtained in pure water (Fig. 1).

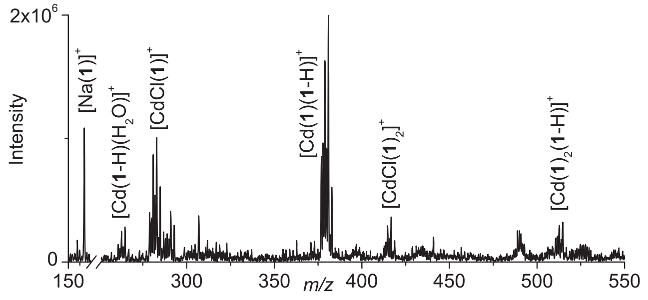

Fig. 7. Positive mode ESI mass spectrum in the range *m/z* 150–550 of malic acid (**1**, 5×10^{-3} mol L^{-1}) and $CdCl_2$ (5×10^{-4} mol L^{-1}) in a mixture of water and soil solution (1:1), pH 6.2.

The pH value of the solution significantly influences the stability of coordination complexes [16,37]. The pK_{a1} and pK_{a2} of malic acid are 3.4 and 5.2 [38]. Most of the measured solutions had a pH value of about 6 (pure water solution with 5×10^{-5} mol L^{-1} $CdCl_2$ and 2.5×10^{-4} mol L^{-1} malic acid, tap water solution with 2.5×10^{-5} mol L^{-1} $CdCl_2$ and 5×10^{-4} mol L^{-1} malic acid, 10^{-6} mol L^{-1} KCl solution with 5×10^{-5} mol L^{-1} $CdCl_2$ and 5×10^{-4} mol L^{-1} malic acid and a soil solution with 5×10^{-4} mol L^{-1} $CdCl_2$ and 5×10^{-3} mol L^{-1} malic acid). The pure water solution with 5×10^{-4} mol L^{-1} $CdCl_2$ and 5×10^{-3} mol L^{-1} malic acid (Fig. 1) had a pH value of 3.5. Considering the overall lower intensity of one order of magnitude diluted solution (Fig. 3) than in concentrated solution (Fig. 1) the intensities of each complexes can be compared. In acidic pH the deprotonation of malic acid is hindered compare to neutral pH. This fact is demonstrated by the lower abundances of $[Cd(\mathbf{1}\text{-H})(\mathbf{H_2O})]^+$ (almost five times) and $[Cd(\mathbf{1}\text{-H})(\mathbf{1})]^+$ (about two times less) in pH 3.5 (Fig. 1) compared in pH 6 (Fig. 3). We also briefly explored more extreme variations of the pH, but both upon addition of HCl to pH = 2.5 and of KOH to pH = 8.5, respectively, the ESI process itself seems to be disturbed and no Cd-containing signals were observed anymore.

4. Conclusion

Electrospray ionization mass spectrometry reveals a high tendency of cadmium(II) ions to form complexes with malic acid, of which the monocation $[Cd(\mathbf{1}\text{-H})(\mathbf{1})]^+$ is reasonably well suited for detection of these species in soil solution. Additional species include contact-ion pairs with the counterion used, e.g. $[CdCl(\mathbf{1})]^+$. Complexes of Cd(II) and malic acid can be detected also in samples prepared upon addition of KCl, as an example of a common base electrolyte influencing the speciation, tap water, and an authentic soil solution from forest soil. More extreme pH values are not tolerated, however, and appear to cause a collapse of the ESI process. Under electrospray conditions, malic acid can be transformed via loss of either CO_2 or "CH_2O_2" into smaller acids. These findings are important with respect to environmental chemistry as well as for extended applications of direct mass-spectrometric sampling in analytical chemistry. Specifically, ESI-MS can be used for the identification of cadmium complexes with malic acid in environmental samples, where this LMWOA is one of the most ubiquitous root exudates and plays an important role in metal uptake by plants, which is currently studied in the context of the phytoremediation of contaminated soils.

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