2 Metal Speciation, Chelation and Complexing Ligands in Plants

A. Pohlmeier

Institut für Chemie und Dynamik der Geosphäre 7, Forschungszentrum D-52425 Jülich, Germany

2.1 Introduction

Most transition metal ions and some main group metal ions form complexes with small (Cl⁻, carboxylic acids, amino acids) and macromolecular organic substances (proteins, DNA, polysaccharides) present in the xylem and phloem of plants (Łobinski and Potin-Gautier 1998). In the first section of this chapter some remarks and definitions concerning the aqueous chemistry of metal ions will be given to facilitate further reading. The following sections present a brief outline of theories describing the nature of the coordination bond, the basic thermodynamics of complexation, the hydrolysis and chelation of metal ions and the reactions with important groups of ligands present in plants. The chapter will close with an overview of some special aspects relevant for the understanding of complexation reactions at macromolecules and the reaction mechanism of complex formation.

2.2 Terminology and Definitions

Most of the metal ions forming complexes may exist in aqueous solution in different oxidation states. Under environmental conditions, i.e. at moderate pH-values and under slightly oxidating conditions, +1 to +3 are the most usual formal oxidation states for the metal ions concerned in the context of this book. Some important exceptions are Mo⁶⁺, which exists in the natural environment as stable MoO₄²⁻ ions, forming no complexes with anionic ligands present in plants, and V⁴⁺, present in most cases as VO²⁺, forming complexes with ligands. The
most stable oxidation state of chromium and iron is +3. However, due to their strong tendency to hydrolyze at moderate pH-values (see below), these ions exist as (poly)hydroxo species or as unsoluble minerals.

In the following, when no special metal ions are considered, complex-forming metal ions will be termed as $M^{\text{+}}$. Metal ion complexes, often also termed as coordination compounds, are formed by at least two partners: the central metal ion, which is generally $M^{\text{+}}$ and the ligand, abbreviated in the following as $L^{-}$. In most cases one metal ion binds at least four ligands, which can be identical, as in the case of the hexaquo-complexes $M(H_{2}O)_{6}^{\text{+}}$ or different like $M(H_{2}O)_{4}Cl_{2}$. The coordination number $Z$ is the total number of ligand ions or molecules directly associated with the metal ion. Its value depends on several factors like the size of $M^{\text{+}}$ and $L$ and the specific electron configuration of $M^{\text{+}}$. Table 2.1. gives a survey of the most usual coordination numbers and geometries of some important metal ions. The charge of the complexes can be negative, zero or positive depending on the sum of charges of $M^{\text{+}}$ and all $L$. The stability of metal ion complexes is expressed by means of the equilibrium constant $K$, often also termed the stability constant or complexation constant. This describes the thermodynamic equilibrium state, keeping in mind that at equilibrium, the rates of complex formation and dissociation are equal. The definition is given in section 2.4 of this chapter.

2.3 Chemical Structure of Simple Complexes

Most metal ions (especially the transition metals) form coordination bonds with ligands, which should not be confused with the weaker, mainly electrostatically controlled ion bond, or the stronger covalent bond, typical for organic chemistry, although the borders are not rigid. The binding strength depends on several factors, such as the electron configuration of $M^{\text{+}}$ and $L$ and the relative energy of the atom and molecule orbitals of the free and coordinated partners. Several theories exist describing the nature of the chemical bond between metal ion and ligand on different levels of abstraction. Here only two theories will be outlined, more detailed treatments can be found in textbooks of physical and theoretical chemistry e.g. Gerloch et al. 1994.

2.3.1 Crystal Field Theory

The crystal field theory, developed in the 1930s, is based on the distribution of electrons in the d-shell of metal ions. For example, Ni$^{2+}$ has eight electrons in the 3 d-shell and the higher shells are unoccupied. In the absence of ligands, all five d-orbitals possess the same energy. The ligands are placed in a certain symmetry around the central metal ion and so exert a varying influence on d-orbitals of different symmetry. For example, imagine the Ni$^{2+}$-ion octahedrally