Available online at www.sciencedirect.com
ScienceDirect
Coordination Chemistry Reviews 252 (2008) 1108–1120
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

Review

Formation and stability of phytate complexes in solution

Francesco Crea, Concetta De Stefano, Demetrio Milea, Silvio Sammartano *

Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, Salita Sperone 31, I-98166 Messina (Vill. S. Agata), Italy

Received 4 June 2007; accepted 15 September 2007
Available online 19 September 2007

Contents

Abstract

1,2,3,4,5,6 hexakis (di-hydrogen phosphate) myo-inositol, best known as phytic acid, is a very important molecule from a biological, environmental and technological point of view. For a thorough understanding of phytate properties and the mechanisms involving this ligand, a careful study of its acid–base behavior and of the formation and stability of its complexes in solution is necessary. Unfortunately, regarding the thermodynamic data on phytate complexes in solution, some are lacking, while some others exhibit large discrepancies between different authors. This motivated a detailed evaluation of the literature on this topic, aimed at identifying the most accurate data on phytate coordination chemistry in solution. This review presents the results of this, reporting and analyzing the most significant thermodynamic parameters published for both phytate protonation and complex formation with several metal and organometal cations, as well as polyammonium ligands.

Keywords: Phytate; Protonation; Metal complexes; Organometal complexes; Polyammonium complexes; Thermodynamic parameters

1. Introduction

1,2,3,4,5,6 hexakis (di-hydrogen phosphate) myo-inositol (Fig. 1), best known as phytic acid, was first identified in 1855 [1]. Phytates, its salts (the completely deprotonated form is denoted in this work by Phy^{12-}), are widely present in nature (plants, animals and soils [2]), mainly as calcium, magnesium

* Corresponding author. Tel.: +39 090 393659; fax: +39 090 392827.
E-mail address: ssammartano@unime.it (S. Sammartano).

0010-8545/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2007.09.008

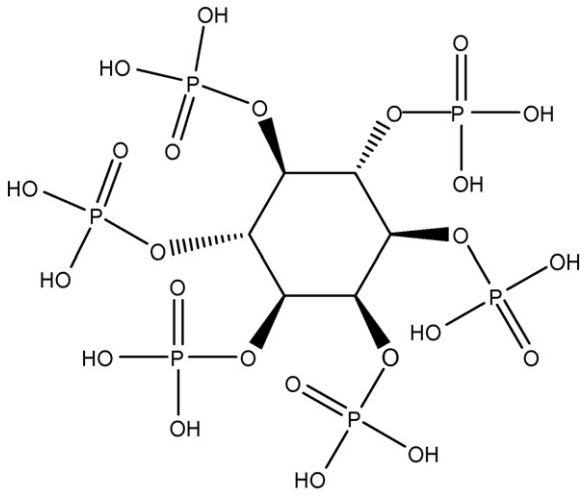

Fig. 1. Basic structure of phytic acid.

and potassium mixed salts (also called phytines) [3]. The existence of this compound in seeds was first reported in 1903 [4] and it is now accepted as being ubiquitous among plant seeds and grains, comprising 0.5–5% (w/w) [2]. On the other hand, although the first report that phytate is present in animal cells appeared in 1941 (which turned out to be a case of mistaken identity) [5], it only became clear in the late 1980s and 1990s that it is also always present in eukaryotic species (typically being the most abundant inositol phosphate in cells) [6]. As a result of this widespread occurrence in nature, its important biological activity and the high number of applications, over the last century it has been the subject of investigation for many scientists in different fields, amply demonstrated by the huge number of papers, reviews and books that have been published (see, for example, references in some recent and past books and reviews [1–3,5–12]). New functions, properties and applications of phytate are being regularly discovered and reported in literature (see, e.g., some papers published in 2007 [13–17]). Here it suffices to say that it modifies the bioavailability of several metal ions (such as calcium, iron, zinc, copper: see, e.g. [18–22] and references therein); it is regarded as the primary storage form of both phosphate and inositol in plant seeds and grains (see, also [23,24] and references therein); it has been reported to be an antioxidant (see also [8,25–29]); it shows marked anticarcinogenic/antineoplastic properties (e.g. [28,30–35]); it may reduce and prevent kidney stone formation [36,37] and it plays key roles in a number of crucial physiological activities, other than in the treatment of different pathologies (thoroughly reviewed, e.g., in Refs. [2,5,6,11]). Among its industrial and/or technological applications (some of them reviewed in [1]), of particular note is the use of phytates in environmental remediation problems, such as the immobilization and in situ treatment of soils contaminated by many metals (including heavy metals and radionuclides, see, e.g. [38–45]).

Most of these phytate properties and applications are significantly influenced by its particular behavior in solution (primarily aqueous media, such as biological fluids, natural and waste waters, “soil solutions”), where it strongly interacts with many metal and non-metal ions, proteins and starch, mainly by electrostatic interactions [1,2,5,11]. Moreover, the peculiar characteristics of its structure allow this ligand to assume two different conformations. While the hexaorthophosphate structure of phytic acid proposed by Anderson [46] has been accepted since the late 1960s [47], many studies have been carried out during the last decades to understand better which phytate conformational states predominate in solution (e.g. [4,48–52]). It transpires that, depending on the experimental conditions, this ligand may exist in solution either in the so-called equatorial conformation in which one phosphate group is oriented in the axial position and five are in the equatorial (1-ax/5-eq), or in the inverted axial conformation (5-ax/1-eq). Various techniques, including potentiometry [49], Raman spectroscopy [48], ^{1}H NMR [49–52], ^{13}C NMR [48,49] and ^{31}P NMR spectroscopy [4,48,49,52], and molecular modeling [51] have been used to probe phytate conformational preferences. These works have demonstrated that the conformation in aqueous solutions depends on many parameters, such as pH, ionic strength, ionic medium (mainly due to the nature of the cation in the supporting electrolyte). According to one of the most recent of these papers [51], in which the effect of alkali metal ions on the conformation adopted by phytic acid was also investigated, this ligand exists at pH < 9 in the sterically unhindered 1ax/5eq form, and at pH > 9.5 in the sterically hindered 5ax/1eq form. Moreover, these authors showed that at pH 5.0, phytic acid adopts the 1ax/5eq form regardless of the alkali metal cation present as counter ion. On the contrary, at pH 11, the exclusive presence of the 5ax/1eq form was observed with Na^+, K^+, Rb^+, Cs^+, whilst with Li^+ ions the two conformations are simultaneously present.

For all the above-cited reasons, to gain a thorough understanding of phytate properties and the mechanisms involving this ligand, a careful study of its acid base behavior and of the formation and stability of its complexes in solution is necessary. After some years of studies on this direction, we realized that, regarding the thermodynamic data on phytate complexes in solution, some are lacking, while some others exhibit large discrepancies between different authors. This motivated a detailed evaluation of the literature on this topic, aimed at identifying the most accurate data on phytate coordination chemistry in solution. This review presents the results of this, reporting and analyzing the most significant thermodynamic parameters published for both phytate protonation and complex formation with several metal and organometal cations (some protonation and complex formation constants are reported in Tables 1 and 2, respectively), as well as other organic ligands. Potentiometry and multinuclear NMR have been the main instrumental techniques used for the determination of stability constants, as recommended by IUPAC [53], while calorimetry has been applied in the determination of protonation and complex formation enthalpies.

2. Acid–base properties

Compared to the large number of papers published on phytate properties and applications, relatively few report quantitative data on the acid–base behavior of this ligand [4,18,22,48,49,54–68], despite being well known that acid–base