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Complex formation between phytic acid and divalent metal ions: a solution equilibria and solid state investigation

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Abstract An investigation on the complex formation equilibria between divalent metal ions Me (with Me=Mn, Co, Ni, Cu, Cd, and Pb) and phytic acid ($H_{12}L$) is presented. Experiments were performed through a potentiometric methodology by measuring, at 25 °C, the proton and, in some cases (Cu^{2+} , Cd^{2+} , and Pb^{2+}), also the metal ion activity at equilibrium in solutions containing, besides the metal and the ligand, 3 M $NaClO_4$ as the ionic medium. Unhydrolyzed solutions of the metal ion at millimolar concentration levels were titrated with solutions of about 10 mM sodium phytate, until the formation of a solid phase took place (always at $pH \approx 2.5$, except in the case of Cu^{2+} , which formed soluble complexes up to $pH \approx 3.3$). Coulometry was employed to produce very dilute solutions of either Cu^{2+} , Cd^{2+} , or Pb^{2+} of accurately known composition. The emf data were explained by assuming, in the acidity interval explored, the formation of the complexes of general stoichiometry MeH_3L^{5-} and $Me_2H_3L^{5-}$. Coordination compounds in the solid state were also synthesized and characterized by elemental analysis, thermal analysis, and ICP spectroscopy. The solids had a general stoichiometry $Me_6H_tLCl_{t-x} \cdot x H_2O$, with the following t and x values for each metal investigated: Me ($t; x$) = Mn (4; 2); Co (4; 2); Ni (4; 2); Cu (2; 2.5); Zn (2; 1); Sn (6; 6).

Keywords Phytate · Metal complexes · Potentiometric method · Coulometric method · Thermogravimetric method

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Introduction

Placed at an intermediate position between the simplest anions and the polyelectrolytes, the *myo*-inositol hexakis(dihydrogen phosphate) ($C_6H_6(H_2PO_4)_6$, in the following indicated as $H_{12}L$), also known as phytic acid, represents an extremely appealing molecule. Phytates are important constituents of cereal grains [1]. Owing to the presence of the six phosphate groups in very close proximity, they strongly bind practically any metal ion. Thus, the nutritional availability of dietary metal ions may be dramatically reduced in the presence of phytates [2]. Furthermore, besides their physiological relevance, they have a broad variety of applications as complexing or precipitating agents: in the last two years alone, more than 400 scientific articles have appeared concerning phytic acid and its salts. The applications of Tc(VII)-L complexes in nuclear medicine and of Gd(III)-L complexes as good contrast agents for NMR-imaging in vivo studies [3] make this molecule a ligand of medical interest. Among the main industrial applications it is worth mentioning its use as antioxidant in foods [4, 5], as an inhibitor of plaque formation in tooth paste [6], as an intermediate in the production of special unleaded fuel [7], and as an antirust agent for metal surfaces [8].

Thus, although the first investigations on phytates were carried out in the early twentieth century [9], they still are extensively studied, particularly for their use as chelating ligands, electrochemical sensors, and use in the industrial extraction of rare earths. However, relatively few studies have been reported in the literature concerning the acid-base properties of phytate as well as its complexing capacity towards metal ions [10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20]: this type of equilibrium reaction has been mainly investigated by combining potentiometry and spectrophotometry with NMR and/or calorimetric methods.

Changes in the conformational states of phytic acid as a function of pH were studied through ^{13}C NMR, ^{31}P NMR, and Raman spectroscopic investigations [11, 12].

The dissociation constants of the first four protons of the acid have been poorly determined; however, it seems well established that the phosphate groups behave independently until the net charge on the anion becomes large enough to influence the further release of protons, through an electrostatic effect. The formation of protonated dimers of the anion becomes detectable at total phytate concentrations larger than 10 mM [15].

Among the electrochemical techniques, only potentiometry has been extensively used to determine the formation constants of the metal-phytate complexes; however, only occasionally, ion selective electrodes, other than the glass electrode, were used. The main difficulties encountered in the investigation of solution equilibria involving phytate arise from the large number of protolytic equilibria involved and from the extremely low solubility of the metal complexes. On the basis of preliminary potentiometric and spectrophotometric measurements on Me^{3+} -phytate systems [21], with $\text{Me}=\text{Fe}$, In , Bi , and Cr , it appeared that the species present at equilibrium at millimolar concentrations levels of metal and of phytate in the 1:1 molar ratio, were soluble only at $\text{pH} < 0$. Conversely with ions of +2 charge, at the same concentrations, clear solutions were obtained provided that $\text{pH} < 3.3$. It is evident from the distribution diagram of Fig. 1, that about 90% of the ligand is in the form H_6L^{6-} at these acidities.

The characterization of the solid-state complexes of phytate is based on few thermoanalytical data [20, 22], although the knowledge of the interactions of phytic acid with essential oligoelements and metal ions of environmental interest would certainly take advantage of a combined solid-state and solution equilibrium approach. In the present work, coordination compounds in the solid state containing phytate and Me^{2+} ions, with $\text{Me}=\text{Mn}$, Co , Ni , Cu , Zn , and Sn , have been synthesized. The determi-

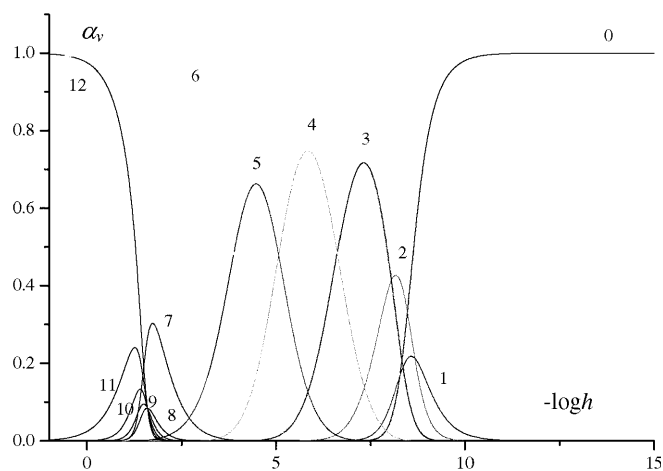


Fig. 1 The protolytic equilibria of phytic acid at 25 °C in 3 M NaClO_4 are presented here in the form of a distribution diagram. The formation of dimers of phytate has not been considered, owing to the low concentrations of the anion employed in this work. The curves have been drawn by using the protonation constants from ref. [15], and assuming that $\text{p}K_{a1} = \text{p}K_{a2} = \text{p}K_{a3} = \text{p}K_{a4} = 1.6$. The number of protons (v) bonded to phytate is indicated on each curve

nation of their stoichiometric composition has been performed through elemental analysis, thermal analysis, and ICP spectroscopy.

Moreover the complex formation equilibria between phytate and some divalent metal ions, namely Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} , have been investigated through a potentiometric methodology. The approach adopted was strictly inspired to the classical principles of equilibrium analysis: thus, the proton, and, in some cases (Cu^{2+} , Cd^{2+} and Pb^{2+}) also the metal ions activity at equilibrium, were measured at 25 °C in diluted solutions.

In the course of the experiments, particular care was devoted to keep the ionic strength of the solutions constant at the 3 M level by the addition of NaClO_4 . Hence, the reference state for the activities was the 3 M NaClO_4 ionic medium, which keeps the activity coefficients' variations of all the reacting species constant provided no more than 10% of the medium ions is replaced.

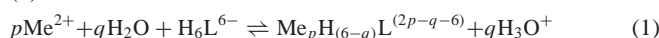
Experimental

Notations

- H analytical proton excess with respect to the zero level constituted by H_2O , Me^{2+} , and H_6L^{6-}
- B analytical concentration of metal ions
- A analytical concentration of phytate
- h concentration of free protons at equilibrium= $[\text{H}^+(\text{aq})]$
- b concentration of free metal at equilibrium= $[\text{Me}^{2+}]$
- a concentration of free ligand at equilibrium= $[\text{H}_6\text{L}^{6-}]$

Solution equilibria

The determination of the equilibrium constant $\beta_{p,q,1}$ of the reaction (1)



has been performed at 25 °C through a potentiometric methodology. This required variation of the analytical concentrations of protons (H), metal ion (B), and phytate (A) in the largest interval possible, consistent with the very low solubility of metal phytates. During the experiments the free protons concentration (h) in the test solution (TS), was determined by means of the galvanic cell (I)



while, in the case of Cu^{2+} , Cd^{2+} , and Pb^{2+} , the free metal ion concentrations (b) were also measured through the cell (II)



In the cells (I) and (II), RE indicates an Ag, AgCl reference electrode, external to the cell but in electrical contact with it through a salt bridge: $\text{RE}=3.000 \text{ M NaClO}_4/0.010 \text{ M NaCl}$, $2.990 \text{ M NaClO}_4/\text{AgCl}$, Ag. In cell (I), GE is a glass membrane electrode, sensitive to the activity of protons; in cell (II), $\text{Me}(\text{Hg})$ was a diluted (about 0.1% for Cd^{2+} and Pb^{2+} , 0.01% for Cu^{2+}) amalgam of the metal in mercury. The free Mn^{2+} , Co^{2+} , and Ni^{2+} concentrations during the experiments were instead calculated from the mass balance equations. An accurate estimate of H , B , and A (better than 0.1%) was pursued during all the stages of the experiments, as it will be evident in the following discussion. This was of paramount importance for a reliable interpretation of the potentiometric data.

The measurements were carried out in the form of potentiometric titrations. Each experiment started by placing in the titration vessel, thermostated at 25.00 ± 0.02 °C, an accurately known volume (V_0) of solution S_0 (the ionic medium), purged by a continuous stream of highly pure nitrogen. The total acidity in S_0 (H_0), was first of all determined by titration with known volumes (V_{T1}) of

a solution T1= H_{T1} M HClO₄, B_{T1} M Me(ClO₄)₂, (3.000- H_{T1} -2 B_{T1}) M NaClO₄. After each addition the emf E_I (mV) of the cell (I) was monitored until it attained a value constant within ± 0.02 mV (usually half an hour). The Nernst equation for the cell (I) at 25 °C, expressed in Eq. (2) with the concentrations in the place of the activities,

$$E_I = E_I^0 + 59.16 \log h + E_j \quad (2)$$

contains the term E_I^0 , a constant that includes, among other quantities, the asymmetry potential of GE, and

$$E_j = -16.8h + 4.5h^2 - 0.55h^3 \quad (3)$$

which is the liquid junction potential that arises at the interphase between TS and the solution of the salt bridge as a consequence of the substitution of the Na⁺ ions with the protons [23]. In the absence of hydrolysis, $h = H$. The (V_{T1} , E_I) data were elaborated by using Gran's method [24], in order to determine E_I^0 and H_0 .

In the case of Cu²⁺, Pb²⁺, and Cd²⁺ the metal was not added with T1 ($B_{T1} = 0$), but produced coulometrically in TS through the electrolysis circuit (III)



in which Me(Hg) was a second cadmium or lead amalgam while AE indicates an auxiliary electrode. To electrolytically produce Cu²⁺ ions, a copper foil proved to be a better choice as anode than the metal amalgam owing to the extremely low solubility of copper in mercury. In the experiments with lead and cadmium, AE = 3.000 M NaClO₄/0.050 M Hg₂(ClO₄)₂, 2.900 M NaClO₄, Hg; the coincidence of the potentials of the amalgam and of the pure metal electrodes, verified preliminarily in separate titrations, demonstrated that mercury cations were not formed in TS. In the case of copper, AE was substituted with a cathode obtained by coating a platinum foil with solid WO₃, into which Na⁺ ions are electro-

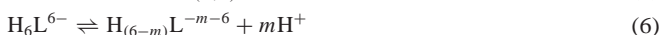
chemically inserted with 100% efficiency [25]. Following the assessment of determine E_I^0 and H_0 , accurately known amounts of Me²⁺ (n_T mol) were produced in situ stepwise through the circuit (III), while the emf of cell (II) (E_{II} (mV)) was recorded after each addition. The acidity of the solutions was high enough to suppress the hydrolysis of the metal ion; hence, in the absence of phytate, $b = B$. The data (n_T , E_{II}) thus collected allowed us to determine, through a Gran plot, the quantity E_{II}^0 appearing in the Nernst equation (Eq. (4)), for cell (II) at 25 °C

$$E_{II} = E_{II}^0 + 29.58 \log b + E_j \quad (4)$$

and to attain a chosen value of B .

Thus, the test solution reached the desired composition, TS: B_0 M Me(ClO₄)₂, H_0 M HClO₄, (3- H_0 -2 B_0) M NaClO₄. The experiment was then completed by titrating TS with known volumes (V_{T2}) of the solution T2: H_{T2} M HClO₄, A_{T2} M Na₁₂L, (3.000- H_{T2}) M NaClO₄, until the incipient formation of a solid phase. After each addition the potentials of the cells (I) and (II) required about 10 min to attain a stable value which remained constant to within ± 0.05 mV, for several hours. This was assumed as a criterion for equilibrium.

The (V_{T2} , E_I) and (V_{T2} , E_I , E_{II}) data collected in the second stage of each potentiometric titration are reported in Table 1 and formed the basis for the evaluation of the formation constants of the metal-phytate complexes. This required us to also consider, besides the reaction (1), the protolytic equilibria of phytate, as represented in the reactions (5) and (6)



of which β_n and χ_m , respectively, represent the equilibrium constants.

Table 1 Survey of the primary data used for the evaluation of the metal-phytate formation constants

Manganese	$V_0 = 60.000 \text{ cm}^3$; $H_0 = 10.730 \text{ mM}$; $B_0 = 9.100 \text{ mM}$; $H_{T2} = -13.224 \text{ mM}$; $A_{T2} = 8.954 \text{ mM}$ (V_{T2}/cm^3 , $-\log h$): 1.000, 1.984; 3.004, 2.014; 6.004, 2.057; 10.026, 2.111; 15.018, 2.176; 20.000, 2.238; 26.000, 2.308; 33.000, 2.386; 40.000, 2.467
Cobalt	$V_0 = 60.006 \text{ cm}^3$; $H_0 = 10.746 \text{ mM}$; $B_0 = 10.015 \text{ mM}$; $H_{T2} = -13.544 \text{ mM}$; $A_{T2} = 8.954 \text{ mM}$ (V_{T2}/cm^3 , $-\log h$): 1.002, 1.984; 2.052, 2.000; 4.008, 2.029; 7.000, 2.073; 10.020, 2.115; 14.996, 2.183; 20.000, 2.249; 25.998, 2.326; 33.004, 2.415
Nickel	$V_0 = 60.012 \text{ cm}^3$; $H_0 = 10.871 \text{ mM}$; $B_0 = 10.061 \text{ mM}$; $H_{T2} = -13.244 \text{ mM}$; $A_{T2} = 8.799 \text{ mM}$ (V_{T2}/cm^3 , $-\log h$): 1.004, 1.979; 2.004, 1.994; 4.002, 2.024; 7.012, 2.068; 11.016, 2.124; 15.008, 2.179; 20.000, 2.245; 26.012, 2.322; 33.000, 2.412
Copper	$V_0 = 70.022 \text{ cm}^3$; $H_0 = 14.863 \text{ mM}$; $B_0 = 0.708 \text{ mM}$; $H_{T2} = -13.554 \text{ mM}$; $A_{T2} = 8.949 \text{ mM}$ (V_{T2}/cm^3 , $-\log h$, $-\log b$): 1.520, 1.813, 3.159; 2.002, 1.820, 3.161; 3.006, 1.833, 3.167; 4.998, 1.859, 3.179; 8.002, 1.895, 3.197; 11.002, 1.932, 3.214; 14.998, 1.980, 3.239; 20.000, 2.038, 3.266; 26.000, 2.103, 3.297 $V_0 = 70.000 \text{ cm}^3$; $H_0 = 2.736 \text{ mM}$; $B_0 = 1.510 \text{ mM}$; $H_{T2} = -13.760 \text{ mM}$; $A_{T2} = 8.941 \text{ mM}$ (V_{T2}/cm^3 , $-\log h$, $-\log b$): 0.502, 3.018, 2.825; 1.004, 3.072, 2.830; 2.004, 3.179, 2.840; 4.000, 3.402, 2.865; 7.000, 3.661, 2.916; 10.022, 3.817, 2.973; 14.002, 3.934, 3.047; 19.008, 4.020, 3.132; 25.032, 4.084, 3.220; 32.134, 4.134, 3.311
Cadmium	$V_0 = 59.994 \text{ cm}^3$; $H_0 = 17.290 \text{ mM}$; $B_0 = 3.350 \text{ mM}$; $H_{T2} = -13.752 \text{ mM}$; $A_{T2} = 8.952 \text{ mM}$ (V_{T2}/cm^3 , $-\log h$, $-\log b$): 0.500, 1.770, 2.467; 1.006, 1.778, 2.472; 2.000, 1.793, 2.481; 4.006, 1.823, 2.500; 7.014, 1.866, 2.527; 10.992, 1.921, 2.562; 15.002, 1.975, 2.595; 20.000, 2.041, 2.633; 26.002, 2.119, 2.679
Lead	$V_0 = 70.000 \text{ cm}^3$; $H_0 = 16.693 \text{ mM}$; $B_0 = 1.150 \text{ mM}$; $H_{T2} = -13.524 \text{ mM}$; $A_{T2} = 8.947 \text{ mM}$ (V_{T2}/cm^3 , $-\log h$, $-\log b$): 1.010, 1.929, 2.950; 2.000, 1.946, 2.960; 4.020, 1.977, 2.976; 7.010, 2.021, 3.006; 10.018, 2.063, 3.033; 13.006, 2.107, 3.064; 16.012, 2.149, 3.091; 20.000, 2.206, 3.148; 25.036, 2.272, 3.205; 30.772, 2.355, 3.279 $V_0 = 60.000 \text{ cm}^3$; $H_0 = 17.428 \text{ mM}$; $B_0 = 0.999 \text{ mM}$; $H_{T2} = -13.740 \text{ mM}$; $A_{T2} = 8.950 \text{ mM}$ (V_{T2}/cm^3 , $-\log h$, $-\log b$): 0.506, 1.813, 3.002; 1.020, 1.820, 3.007; 1.998, 1.836, 3.018; 3.996, 1.864, 3.040; 7.014, 1.906, 3.073; 11.022, 1.958, 3.111; 14.992, 2.010, 3.149

The calculations have been made by using the generalized least-squares program Letagrop-Etitr [26]. The error-carrying variable was chosen to be H ; the program determined the set of equilibrium constants that minimized the function

$$U = \sum (H_{\text{exp}} - H_{\text{calc}})^2 \quad (7)$$

In Eq. (7), H_{exp} was an experimental value while

$$H_{\text{calc}} = h + \sum n\beta_n a h^n - \sum m\chi_m a h^{-m} - \sum \sum q\beta_{p,q,1} a b^p h^{-q} \quad (8)$$

in which a indicates the concentration of H_6L^{6-} . Each $\beta_{p,q,1}$ was determined by using the h and b values determined from the measured E_I and E_{II} through the Eqs. (2) and (4), employing the E_I^0 and E_{II}^0 previously evaluated. The concentration a was calculated from Eqs. (9) or (10) (when h and b were known)

$$a = (B - b) / \left(\sum \sum p\beta_{p,q,1} b^p h^{-q} \right) \quad (9)$$

$$a = A / \left(1 + \sum \beta_n h^n + \sum \chi_m h^{-m} + \sum \sum \beta_{p,q,1} b^p h^{-q} \right) \quad (10)$$

or from both of them. Obviously the accuracy of the (H , B , A , h) or (H , B , A , h , b) data determined those of the constants.

Solid state complexes

The syntheses were carried out by adding a phytate solution to a metal chloride solution; the pH of the ligand solution was initially adjusted to around 0.5. The metal/ligand ratio and the pH at which precipitation started are reported in Table 2.

The solids were washed with distilled water, filtered under vacuum, and dried at 80 °C until constant weight, to remove the hygroscopic water.

Reagents and analysis

HClO_4 stock solutions were prepared diluting the 65% R.P.E. Carlo Erba product without any further purification, since it did not contain significant levels of redox impurities. The analysis, carried out by the classical acid-base titration procedures, using KHCO_3 and methyl red, agreed within $\pm 0.05\%$.

NaClO_4 stock solutions were synthesized from HClO_4 and Na_2CO_3 (R.P.E. Carlo Erba), and analyzed as described by Biedermann [27].

Stock solutions of $\text{Hg}_2(\text{ClO}_4)_2$ were obtained by mixing HgO(s) (R.P.E. Carlo Erba) and Hg(l) , 5 N, furnished by Fluka, in a slight excess of HClO_4 . The stocks were titrated potentiometrically, varying the Hg_2^{2+} concentration by coulometric reduction at a mercury cathode.

Manganese, cobalt, and nickel perchlorate stock solutions were prepared and standardized as described elsewhere [28].

The dodecasodium salt hydrate of phytic acid and the divalent metal chloride salts were purchased from Aldrich Chemical Co., as well as metallic copper (3 N), cadmium (5N8), and lead (5N5).

All the solutions were deoxygenated by purging them with a vigorous nitrogen stream. The gas (99.98%), from cylinders, bubbled through a series of washing bottles containing a Cr(II) reduc-

ing solution, 10% NaOH, 1 M H_2SO_4 , doubly-distilled water, and 3.000 M NaClO_4 so as to saturate it at the same water vapor pressure of TS.

Materials and equipment

All the experiments were carried out into an air box thermostat, capable of keeping the temperature of the solutions at 25.00 ± 0.02 °C.

The high-impedance glass electrodes were supplied by Metrohm; highly precise ± 0.01 mV emf measurements could be made using home-made impedance adaptors.

Ag, AgCl electrodes were prepared according to Brown [29].

A fully automated data acquisition system based on Hewlett-Packard components, combined with the software TITPOT™ pursued by InLab Software House allowed us to control the experiments around the clock.

The automatic burettes employed were Dosimat 715 from Metrohm with a precision of ± 0.004 cm³.

The coulometric circuits were achieved using a Hewlett-Packard DC Power Supply E3612A.

The thermoanalytical curves were obtained using a Perkin-Elmer TGA7 thermobalance (range 20–1000 °C); the atmosphere was either pure nitrogen or air, at a flow rate of 100 cm³ min⁻¹, to evaluate the different behavior in oxidizing conditions; the heating rate was varied between 5 and 40 °C min⁻¹, with the best resolution achieved at a scanning rate of 10 °C min⁻¹.

Results and discussion

Solution equilibria

In Table 3 the formation constants of the complexes of phytic acid with Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} , determined through potentiometric titrations at 25 °C in 3 M NaClO_4 are reported. In the case of Mn^{2+} , Co^{2+} , and Ni^{2+} the measurements have been performed by using only the glass membrane electrode. The pH range explored was limited by the precipitation of a sparingly soluble solid, which did not favor the formation of appreciable amounts of complexes bearing more than two metal ions. The results indicate that the strength of the complexes, in passing from Mn^{2+} to Ni^{2+} , does not change appreciably. In the case of Cu^{2+} , Cd^{2+} , and Pb^{2+} the use of a metal amalgam in addition to the glass electrode furnished the fundamental information represented by the activity of the free metal. While the complex formation mechanism for Cd^{2+} and Pb^{2+} does not change dramatically, the behavior of Cu^{2+} seems anomalous, both for the larger pH range of solubility and for the strength of the complexes.

Solid state complexes

The thermogravimetric (TG) profiles of the solid state complexes of phytic acid with Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Sn^{2+} reported in Fig. 2, were used to determine their stoichiometry.

The main thermal decomposition steps, after the loss of water, are the release of the chloride ions and the decomposition of the aliphatic ring. For all the curves, the final residue does not correspond to the metal oxide because of

Table 2 Experimental conditions for the synthesis of the metal-phytate complexes. The solid phase was obtained by adding dropwise a 5.0 mM solution of Na_{12}L to a 5.0 mM solution of MeCl_2 , 0.3 M HCl. The pH and the metal/ligand ratio at the starting precipitation are reported for each metal ion

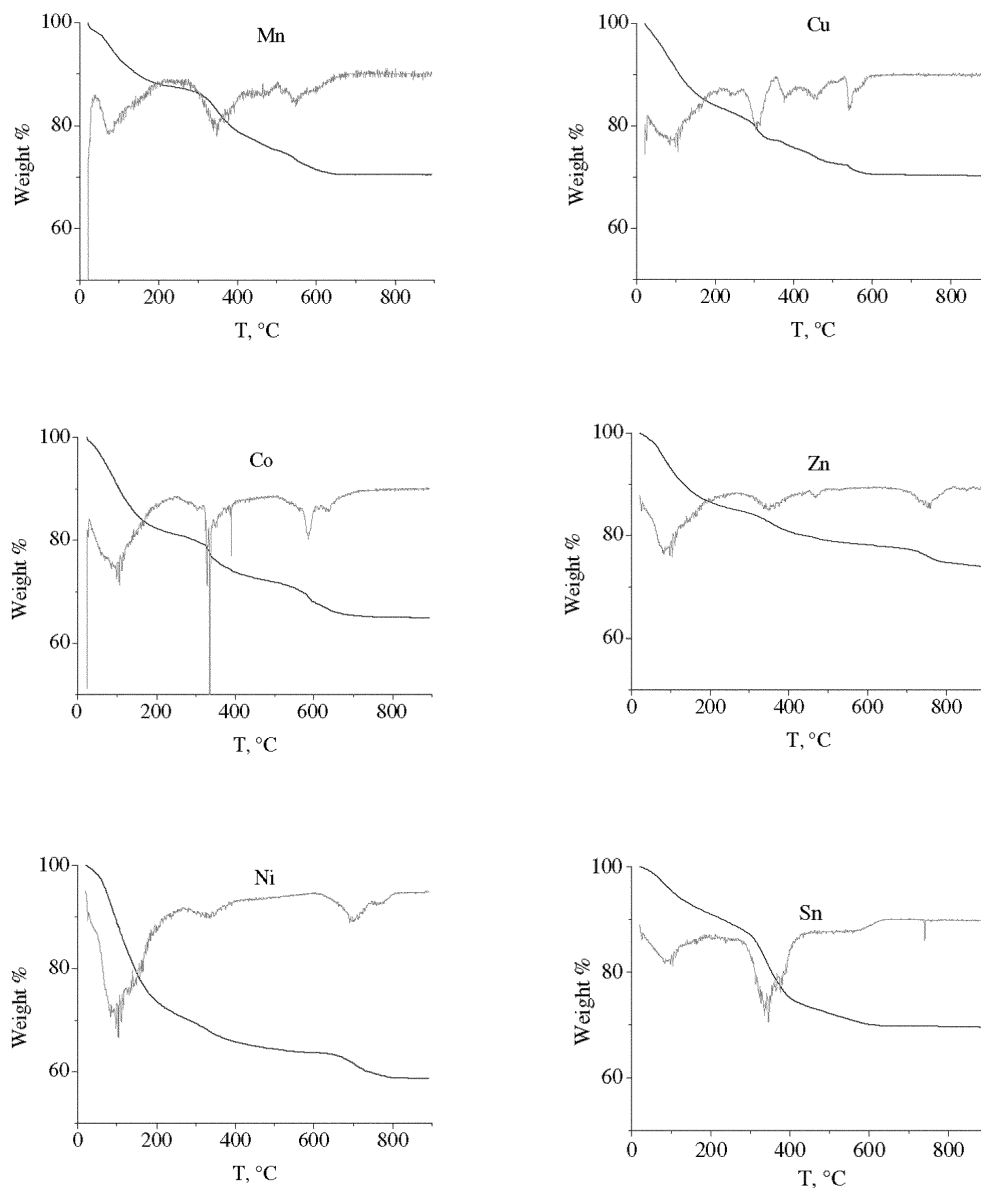
Ion	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Sn^{2+}
pH	6.0	6.2	6.1	4.1	5.4	2.6
B/A	25	33	63	50	25	128

Table 3 Survey of the formation constants of the metal-phytate complexes at 25 °C in NaClO₄ 3 M^a

Ion	Mn ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Cd ²⁺	Pb ²⁺
log($\beta_{1,1,1\pm 3\sigma_{1,1,1}}$)	-0.03±0.04	-0.04±0.02	-0.10±0.02	-1.25±0.05	-0.24±0.0	-0.01±0.08
log($\beta_{2,3,1\pm 3\sigma_{2,3,1}}$)	-3.14±0.04	-3.61±0.07	-3.72±0.08	-6.60±0.06	–	-2.7±0.5
σ (mM)	0.01391	0.00834	0.00765	0.00437	0.01089	0.00679

^aThe equilibrium constant of the reaction $p\text{Me}^{2+} + q\text{H}_2\text{O} + \text{H}_6\text{L}^{6-} \rightleftharpoons \text{Me}_p\text{H}_{(6-q)}\text{L}^{(2p-q-6)} + q\text{H}_3\text{O}^+$ is $\beta_{p,q,1}$, while $\sigma_{\beta_{p,q,1}}$ represents the standard deviation on the constant, σ the standard deviation of the data

Fig. 2 Thermogravimetric profiles of the $\text{Me}_6\text{H}_t\text{LCl}_t \cdot x \text{H}_2\text{O}$ compounds. Scanning rate: 10 °C min⁻¹. Air flow at 100 cm³ min⁻¹



the high stability of the phosphates. The colored powder remaining in the TG crucible at 900 °C (metal phosphate) is stable up to 1000 °C and more, with the decomposition to metal oxide occurring beyond 1300 °C. To define the stoichiometry of the complexes, the third step was considered to be due to the loss of a weight corresponding to C₆H₆, as also shown by the thermogravimetric decomposition of the standard phytic acid; the number of bonded

metals and the number of chlorides for each molecule of phytate was consequently calculated.

Elemental analysis and ICP spectroscopy, whose results are reported in Table 4, confirmed the suggested formula.

The solids show a general formula $\text{Me}_6\text{H}_t\text{LCl}_t \cdot x \text{H}_2\text{O}$ (with $t = 2, 4, \text{ or } 6$): Mn₆H₄LCl₄·2 H₂O; Co₆H₄LCl₄·2 H₂O; Ni₆H₄LCl₄·2 H₂O; Cu₆H₂LCl₂·2.5 H₂O; Zn₆H₂LCl₂·H₂O;

Table 4 Survey of the elemental analysis and ICP spectroscopy results obtained in the determination of the stoichiometry of metal-phytate solid state complexes

Solid	Experimental % (calculated)			
	Elemental analysis			ICP spectroscopy
	O	C	P	Me
Mn ₆ H ₄ LCI ₄ ·2 H ₂ O	36.1 (36.0)	6.4 (6.2)	16.2 (16.1)	28.9 (28.5)
Co ₆ H ₄ LCI ₄ ·2 H ₂ O	35.0 (35.2)	6.1 (6.1)	15.8 (15.8)	29.8 (30.0)
Ni ₆ H ₄ LCI ₄ ·2 H ₂ O	38.2 (38.0)	6.2 (6.1)	15.9 (15.8)	30.0 (29.9)
Cu ₆ H ₂ LCI ₂ ·2.5 H ₂ O	37.0 (37.0)	6.0 (6.3)	16.4 (16.2)	33.0 (33.3)
Zn ₆ H ₂ LCI ₂ ·H ₂ O	36.0 (35.4)	6.4 (6.4)	16.5 (16.4)	34.8 (34.7)
Sn ₆ H ₆ LCI ₆ ·6 H ₂ O	35.0 (35.2)	4.3 (4.4)	11.5 (11.4)	44.0 (43.8)

Sn₆H₆LCI₆·6 H₂O. All the precipitated complexes show a characteristic metal/ligand ratio of 6:1, with a different number of chloride ions, which is probably related to the conditions of the synthesis. The syntheses of the complexes often resulted in mixtures of different compounds, and the 6:1 pure complexes were not easy to obtain: this behavior can be explained by the strong coordination properties of the ligand molecule, and the experimental conditions need to be exactly reproduced.

The coordination of up to six metal ions to phytate in solution occurs within an extremely narrow pH interval, before the formation of a solid phase. Under such conditions, the accuracy of the potentiometric data did not allow us to determine the formation constant of species other than the proposed ones with a sufficiently low standard deviation, although their existence can be reasonably hypothesized.

Looking at the thermogravimetric profiles, the proposed thermal stability scale of the phytate complexes is Zn > Ni ≅ Cu ≅ Co > Mn > Sn. The increasing stability of the precipitated complexes is directly related to the decrease of the number of the chloride ions in the structure, suggesting that the higher stability is reached when all the phosphate groups are deprotonated. However, these conditions were never attained because of the precipitation of the solids already at low pH values. The complexes show a different number of coordinated water molecules: experimentally this number increases with the decreasing thermal stability, and it could also be related to the higher number of chloride ions, thus suggesting the possibility of stronger hydrogen bonding in the tin complex (6 Cl⁻ ions) with respect to the zinc complex (only 2 Cl⁻ ions).

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