Chelates in agriculture

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Abstract

Within the past 20–25 years it has been recognized that many of the micronutrient requirements of plants could be supplied by complexes containing chelated metals. These chelates find uses in a wide variety of agricultural crops such as: corn, bush beans, cucumbers and citrus groves. Applications vary from fertilizer additives and seed dressing to foliar sprays and hydroponics. The chelates themselves have chemical structures that seem to be limited only by the chemists imagination. The critical factors for the use of any of these chelates is the stability constant and the cost to prepare a pound of chelated metal such as iron or zinc. A comparison of costs for a few of the more common chelates indicates a need for agricultural studies on the results of using glucoheptonates for supplying micronutrients.

Almost 100 years ago in 1893 Alfred Werner, in his study of the structure of metal complexes, postulated a ring structure for complexes containing ethylenediamine [1]. In 1920 Morgan and Drew introduced the term chelate for ligands, such as ethylenediamine, with two donor atoms that bond to the same metal atom forming a ring [2]. Many ligands have been found that contain more than two donor atoms that can bond to a central metal atom and form multiple rings. EDTA, ethylenediaminetetraacetic acid, forms many complexes in which 6 atoms bond with the central metal atom. It is understood that a bond is formed in a metal complex when the metal atom has available empty orbitals and reacts with a ligand that contains an atom with an unshared pair of electrons. This is called a Lewis acid-base reaction. The Lewis acid has an empty orbital and the Lewis base donates a pair of electrons into the empty orbital forming a bond. The iron (III) ion reacts with ammonia to form a complex according to the following equation.

$$Fe^{3+} + 6 NH_3 \rightarrow Fe(NH_3)_6^{3+}$$
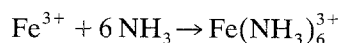
When ethylenediamine is substituted for ammonia, the two nitrogen atoms each donate a pair of electrons thereby forming a chelate.

$$Fe^{3+} + 3 NH_2CH_2CH_2NH_2 \rightarrow$$
$$Fe(NH_2CH_2CH_2NH_2)_3^{3+}$$
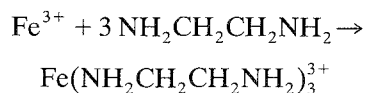
See Fig. 1 for the structure of iron(III) ethylenediamine and other common complexes used for supplying micronutrients to crops. Generally a complex containing five- or six-membered chelate rings is more stable than a similar complex that lacks the chelate rings. This means the chelate will have a larger stability constant than a similar complex containing similar metal ligand bonds but without the chelate rings. The donor atoms can vary considerably considering that a lone pair of electrons is the main requirement, but the most common chelates use nitrogen and/or oxygen. The structure of chelating agents seems to be limited only by the chemist's imagination so we find the literature full of a variety of exotic molecules.

The first use of a chelated metal in a nutrient solution for plants is attributed to a scientist by the name of Jacobson who did the initial work
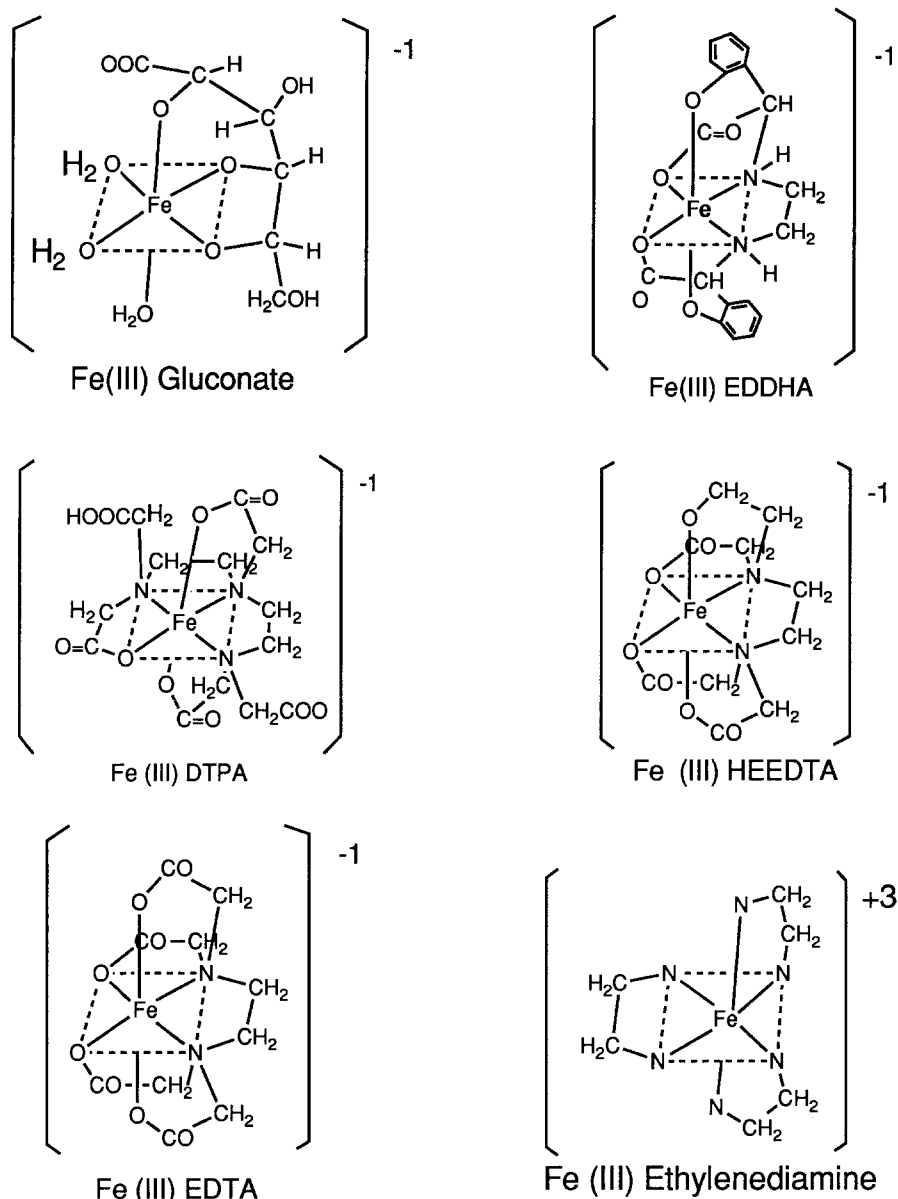
Fig. 1. Complexes.

prior to 1949 [3]. Since that time, a variety of chelated metals have been studied as micronutrients using a considerable number of different chelating agents. In Fig. 1 iron is shown as the chelated metal and in each case the iron is said to be in an octahedral environment. That is, the metal is surrounded by six donor atoms which form an octahedron around it. Ethylenediamine has only two donor atoms so three molecules are required to coordinate to the six positions on the octahedron. EDTA coordinates to all six positions but the gluconate only forms three bonds so the other three positions are taken by water molecules. Table 1 gives the chemical name for the abbreviations used in industry and in this article.

In plant nutrition there are a number of metals that are generally considered essential as mi-

Table 1. Abbreviations of compounds

Abbreviation	Chemical name
EDTA	Ethylenediamine tetraacetic acid
EDDHA	Ethylenediamine di(o-hydroxyphenylacetic acid)
HEEDTA	Hydroxyethyl ethylenediamine triacetic acid
DTPA	Diethylenetriamine pentaacetic acid
Gluconate (GL)	The salt of gluonic acid
Glucoheptonate (GLH)	The salt of glucoheptonic acid

cronutrients. (The most common are iron, manganese, molybdenum, copper, zinc and boron). These metals are required in very small amounts and, in many cases, are harmful if present in large concentrations. A chelating agent that is effective with one metal at a given pH and in a particular soil may not be useful with different metals or at different pH or soil conditions.

The chelating agents that have been studied the most for plant nutrition fall into two categories, aminopolycarboxylates and hydroxycarboxylates. The term carboxylate indicates that these compounds are organic acids. The aminopolycarboxylates include: EDTA, HEEDTA, DTPA, and EDDHA. The hydroxycarboxylates include: citric acid, a tricarboxylate; saccharic acids such as manaric acid, a dicarboxylate; gluconic acid, a monocarboxylate; and glucoheptonic acid, another monocarboxylate. Many of these chelating agents, both the aminopolycarboxylates and the hydroxycarboxylates, are actually used as the sodium or potassium salts rather than as the free acid.

The various chelated metals are supplied to plants as micronutrients generally as foliar sprays or by direct soil application. (Seed dressing has been used in a few instances). The foliar spraying technique is not feasible with some crops because of the lack of spraying equipment or because of the possibility of staining or otherwise damaging the crop. Some of the problems associated with applying chelated micronutrients to the soil are related to the effects of pH, bicarbonate and the presence of other metal ions in the soil. Calcareous soils usually have a pH above 8 due to the presence of calcium carbonate. The hydroxide ion concentration in such soils is high enough to convert any free iron to iron hydroxide which is quite insoluble (the stability constant for iron (III) hydroxide is 38.57) [4]. In the presence of bicarbonate, the HCO_3^- and OH^- ions appear to compete for the empty orbitals of iron and in many cases displace the original chelating agent to form a more stable complex. If chelated iron is added to calcareous soil and the particular chelating agent used forms a more stable chelate with calcium than with the iron, the chelate will release the iron which may then form insoluble iron hydroxide in the basic soil. Some iron chelates are very stable at a pH of 4 but lose their stability when the pH is very much above 7.

One of the problems facing the user today is the fact that some products labeled x% chelated metal actually contain x% metal but only a portion of the metal is actually chelated. Some states are now requiring that the label state what percentage of the metal is free and what percentage is actually chelated. The state of Florida requires that chelated iron sold there must undergo a test to show that the material meets the specifications on the label. More states should follow Florida's lead

One measure of the effectiveness of a given chelate is the stability constant expression:

$$K = \frac{[\text{metal chelate}]}{[\text{metal}][\text{chelate}]}$$

This expression is defined from the equilibrium equation

$$\text{metal} + \text{chelate} \Leftrightarrow \text{metal chelate}$$
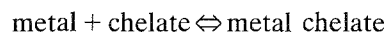
The most common means of presenting this information is in the form of the logarithm to the base 10 of the value of K. The larger this value, the greater is the stability of the complex. Table 1 lists the log K values for some of the common chelates used for providing micronutrients.

Table 2.

Chelating Agent	Fe^{3+}	Fe^{2+}	Zn^{2+}	Log K Cu^{2+}	Mn^{2+}	Ca^{2+}	Ref.
EDTA	25.0	14.27	14.87	18.70	13.81	11.0	[5]
EDDHA	33.9	14.3	16.8	23.94	—	7.20	[5]
HEEDTA	19.6	12.2	14.5	17.4	10.7	8.0	[6]
Citrate	11.2	4.8	4.86	5.90	3.70	4.68	[5]
Gluconate (GL)	37.2	1.0	1.70	36.6	—	1.21	[5]

The large value for iron (III) hydroxide (log K = 38.57 Handbook of Chemistry and Physics) indicates that the iron (III) EDTA chelate in alkaline solution will dissociate and the EDTA will be replaced by hydroxyl ions. The iron (III) EDDHA will be more stable because of its larger stability constant (log K = 33.9). This is consistent with the data presented by Arthur Wallace in his book "A Decade of Synthetic Chelating Agents in Inorganic Plant Nutrition" and other publications [7a,b,c]. Continuing the comparison of stability constants from Table 1, gluconate is a better chelating agent for iron (III) than EDDHA. The small stability constant for calcium gluconate and the fact that the metal gluconates are more stable in alkaline solution than in acidic solution indicates that iron (III) gluconate is less likely to dissociate to replace the iron (III) with calcium. In the case of iron (III) EDTA and iron (III) EDDHA, studies indicate that displacement of iron (III) by calcium begins at about pH 5.5 and 9.9 respectively [8].

Whistler has looked at the role of sugar acid chelates in agriculture and has compared glucoheptonate with a variety of the aminopolycarboxylates [8]. His conclusion is that, for many applications, the sugar acids are superior to the aminopolycarboxylates because of price and particularly in applications to alkaline soil. The ability of sugar acids to form water-soluble complexes with metal ions arises from the ability of carboxyl and hydroxyl groups to bind cations in a ring through coordinate covalent bonds. In the acid or neutral condition, the metal cations form a loose complex with the hydroxyl groups, however, in the alkaline condition, the proton dissociation of the hydroxyl groups form the alkali alcoholate which forms strong coordinate covalent bonds with metal cations.

The stability constants of metal glucoheptonates are not available for comparison but studies seem to indicate that the glucoheptonate is a better chelating agent for heavy metals than the other chelating agents listed in Table 1. Holstein showed that iron (III) glucoheptonate is effective in most soil applications [9] and Shishniashvili et al showed that, in alkaline medium, glucoheptonate has greater complex-forming ability than gluconate with iron (III) [10]. Sugar acid chelating agents, such as gluconate or glucoheptonate, are more stable at higher pH levels as opposed to aminopolycarboxylates that tend to decrease in stability as the pH is raised. This means that the sugar acid chelating agents are effective even in alkaline soils and studies have shown that chlorosis due to iron deficiency in calcareous soils is corrected by addition of iron (III) glucoheptonate. The large stability constant for iron (III) EDDHA bears out the studies that show this complex is also very effective for chlorosis control in calcareous soil. The relatively high cost of the product limits its use to high value crops. In general, the hydroxycarboxylate sugar acids are cheaper and can therefore be considered for use on lower value crops [11, 12].

How does a user go about choosing a chelated micronutrient assuming that there is no free or unchelated metal in any of the possible chelates and that all of the choices will actually be effective for the type application planned. If all other factors are equal then price should be the determining consideration and the user should calculate the cost to purchase one pound of the metal. For example, if chelated iron is available at $0.30 per pound and it is 5.5% Fe and weighs 11.5 pounds to the gallon, then one gallon would contain 11.5 lb/gal × 0.055 = 0.633 lb Fe/gal. The cost of one gallon of the chelate would be

Table 3. Prices for the purchase of one pound of chelated metal[a,b]

Chelate	Density	% Metal	Price per pound of chelate	Price per pound of chelated metal
FeEDTA s	—	13% Fe	$2.40/lb	$18.50/lb Fe
FeDTPA s	—	11% Fe	$3.01/lb	$27.40/lb Fe
FeHEEDTA s	—	9% Fe	$2.11/lb	$23.40/lb Fe
ZnEDTA s	—	14% Zn	$2.15/lb	$15.40/lb Zn
MnEDTA l	—	12% Mn	$2.40/lb	$20.00/lb Mn
CuEDTA s	—	14.5% Cu	$3.07/lb	$21.20/lb Cu
MgHEEDTA s	—	4% Mg	$2.03/lb	$50.80/lb Mg
FeEDDHA s	—	6% Fe	$10.80/lb	$180.00/lb Fe
FeGLH l	10.85 lb/gal	6% Fe	$0.25/lb	$4.20/lb Fe
CuGLH l	10.5 lb/gal	8% Cu	$0.45/lb	$5.60/lb Cu
ZnGLH l	11.4 lb/gal	10% Zn	$0.40/lb	$4.00/lb Zn
MnGLH l	10.4 lb/gal	5% Mn	$0.40/lb	$8.00/lb Mn
ZnEDTA l	10.8 lb/gal	6.5% Zn	$0.643/lb	$9.90/lb Zn
MnEDTA l	11.2 lb/gal	6% Mn	$0.785/lb	$13.10/lb Mn
FeHEEDTA l	11.6 lb/gal	4.5% Fe	$0.68/lb	$15.10/lb Fe
CuEDTA l	10.5 lb/gal	7.5% Cu	$1.105/lb	$14.70/lb Cu
MgEDTA l	10.2 lb/gal	2.5% Mg	$0.76/lb	$30.40/lb Mg
CaEDTA l	9.9 lb/gal	3% Ca	$0.73/lb	$24.30/lb Ca

[a] An s or l following the chelate designation indicates either solid or liquid.
[b] GLH represents the glucoheptonate.

11.5 lb/gal × $0.30/lb = $3.45/gal. The price per pound would then be $3.45/gal divided by 0.633 lb Fe/gal = $5.45/lb Fe. If the chelated metal is a solid the price per pound divided by the percentage of metal expressed as a decimal (6% = 0.06) equals the cost for a pound of the metal. Table 3 compares the cost to purchase one pound of chelated metal for various liquid and solid chelates. The prices are accurate for June 1989.

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