GrowGreen FERTILISER

TECHNICAL REVIEW — PLANT NUTRITION

Amino Acids as Metal-Chelating Agents

Properties and Comparison with Conventional Chelators

How amino acids bind nutrient metals, how they compare with EDTA, DTPA, EDDHA, lignosulfonates and gluconates, and why binding strength alone does not determine nutrient delivery.

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1. Introduction.

Complexing agents are used in fertilisers to influence the chemical form and availability of metal nutrients. Their value depends on retaining a useful nutrient supply during application and allowing the plant to acquire and utilise that nutrient. Binding strength is one part of this process; solution chemistry, formulation and plant uptake mechanisms also matter.

Amino acids are of particular interest because they can bind metals and, once available for uptake and metabolism, provide a biologically useful ligand. This article examines their binding properties alongside EDTA, DTPA, EDDHA, lignosulfonates and gluconates. It follows the nutrient from formulation and application to release and uptake, distinguishing measured chemical stability from demonstrated nutritional performance.

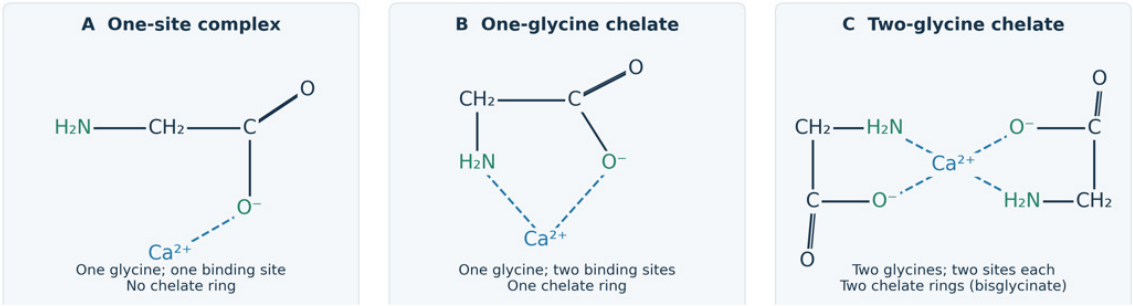
2. Fundamentals of metal–amino acid complexation and chelation.

Complexation occurs when a metal ion binds to a molecule or ion known as a ligand. Amino acids can act as ligands because they contain atoms capable of forming these bonds. Common binding sites include the nitrogen of the amino group and oxygen atoms of the carboxyl group (Figure 1). Some amino acids also have side chains that provide additional binding sites.

Chelation is a particular type of complexation in which two or more binding sites within the same ligand attach to the same metal ion, forming a ring-like structure. A single amino acid can therefore form a chelate if it binds through two suitable sites, such as the amino nitrogen and a carboxyl oxygen. Chelates can also contain two amino acid molecules per metal ion (e.g. calcium bisglycinate, Figure 1). The definition reproduced by Ashmead (2012) allows one to three amino acid molecules per metal ion, preferably two.

These interactions depend on the metal, the amino acid and the surrounding solution. pH affects whether the binding groups carry hydrogen ions, which influences their ability to bind metals. The relative amounts of metal and amino acid also matter. Andreoli *et al.,* (1980) demonstrated that zinc and glycine can form several complexes in aqueous solution, containing different numbers of glycine ligands per zinc ion. A fertiliser containing both ingredients may consequently contain a mixture of bound and unbound forms rather than one uniform compound (Andreoli *et al.,* 1980).

Figure 1. Glycine-calcium complexation and chelation.



For fertiliser use, binding can help maintain a metal in solution under suitable conditions, but simply mixing amino acids with a metal salt does not establish that the metal is fully chelated. The extent and stability of binding must be considered under the conditions of formulation and application. Likewise, demonstrating complex formation establishes a chemical interaction; improved plant uptake requires separate experimental evidence.

3. Binding affinity and stability of amino acid–metal complexes.

Different amino acids vary in their ability to bind mineral nutrients. Their differing chemical structures produce different affinities for mineral nutrients, so their contribution depends on the individual amino acids involved.

Table 1 expresses metal–amino acid binding through formation constants. K_1 describes attachment of the first amino acid molecule to a metal ion, while K_2 describes attachment of a second molecule to the existing complex. β_2 describes the overall formation of the species containing two amino acid molecules and equals $K_1 \times K_2$. For a species containing only one amino acid molecule, the overall constant β_1 is identical to K_1.

Table 1. Selected stability constants of amino acid complexes with divalent nutrient metals at 25°C, compiled from Ashmead (2012). The asterisk (*) marks a calculated value, rather than one printed directly in the source.

Amino acid	Metal	log K_1	log K_2	log β_2
Glycine	Ca^{2+}	1.38	—	—
Serine	Ca^{2+}	≈0.50	—	—
Aspartate	Ca^{2+}	1.60	—	—
Glutamate	Ca^{2+}	2.05	—	—
Glutamine	Ca^{2+}	0.18	—	—
Glycine	Mg^{2+}	3.44	3.01	6.45*
Cysteine	Mg^{2+}	<4	—	—
Aspartate	Mg^{2+}	2.43	—	—
Glutamate	Mg^{2+}	1.90	—	—
Asparagine	Mg^{2+}	—	—	≈4.00
Proline	Mg^{2+}	—	—	<4
Glycine	Mn^{2+}	3.44	—	—
Cysteine	Mn^{2+}	4.10	—	—
Aspartate	Mn^{2+}	3.74	—	—
Glutamate	Mn^{2+}	3.30	—	—
Lysine	Mn^{2+}	2.00	—	—
Histidine	Mn^{2+}	—	—	7.74
Asparagine	Mn^{2+}	—	—	≈4.50
Proline	Mn^{2+}	—	—	5.50
Glycine	Fe^{2+}	4.30	3.50	7.80*
Cysteine	Fe^{2+}	—	—	11.77
Serine	Fe^{2+}	—	—	7.00
Histidine	Fe^{2+}	—	—	9.30
Lysine	Fe^{2+}	4.50	—	—
Glutamate	Fe^{2+}	4.60	—	—
Asparagine	Fe^{2+}	—	—	6.50
Proline	Fe^{2+}	—	—	8.30

Amino acid	Metal	log K_1	log K_2	log β_2
Glycine	Zn^{2+}	5.52	4.44	9.96*
Cysteine	Zn^{2+}	9.86	8.84	18.70*
Aspartate	Zn^{2+}	5.84	4.31	10.15*
Glutamate	Zn^{2+}	5.45	4.01	9.46*
Histidine	Zn^{2+}	—	—	12.88
Lysine	Zn^{2+}	—	—	7.60
Arginine	Zn^{2+}	—	—	7.80
Asparagine	Zn^{2+}	—	—	8.70
Proline	Zn^{2+}	—	—	10.20
Glycine	Cu^{2+}	8.62	6.97	15.59*
Serine	Cu^{2+}	—	—	14.54
Aspartate	Cu^{2+}	8.57	6.78	15.35*
Glutamate	Cu^{2+}	7.85	6.55	14.40*
Histidine	Cu^{2+}	—	—	18.33
Lysine	Cu^{2+}	—	—	13.70
Arginine	Cu^{2+}	—	—	13.90
Asparagine	Cu^{2+}	—	—	14.90
Proline	Cu^{2+}	—	—	16.80

These constants are presented as base-10 logarithms to make their wide range easier to display. An increase of one logarithmic unit represents a tenfold increase in the corresponding constant. Higher values indicate more favourable association when the same type of constant is compared under equivalent conditions.

The zinc entries in Table 1 illustrate how binding strength differs between amino acids. Glycine has a reported log K_1 of 5.52, whereas cysteine has a reported value of 9.86. The higher value for cysteine suggests stronger association of one cysteine molecule with zinc than of one glycine molecule with zinc. Similarly, the reported first-step values for zinc binding to aspartate and glutamate are 5.84 and 5.45, respectively. These comparisons illustrate differences in affinity, although the measurement conditions are not identical or fully specified and therefore do not establish an exact ranking (Ashmead, 2012).

For zinc–glycine, log K_2 is 4.44 and describes attachment of a second glycinate molecule to zinc that already has one attached. Its lower value than log K_1 indicates that the second attachment is less favourable than the first. If the two-glycinate complex loses one ligand, zinc remains bound to the other; it has not become free zinc. The overall constant β_2 accounts for both binding steps, with log β_2 calculated as 5.52 + 4.44 = 9.96. This larger number does not make the second attachment stronger: it describes the complete association of zinc with two glycinate molecules, rather than either attachment individually. Conversely, complete dissociation requires loss of both ligands, whereas loss of the second ligand alone is governed by the reverse of the K_2 equilibrium.

4. Comparison with other agricultural chelating and complexing agents.

Amino acids are one of several types of compounds used to bind mineral nutrients in fertilisers. Other commonly used agents include EDTA, DTPA, EDDHA, lignosulfonates and gluconates. Their chemical structures influence which metals they bind, the strength of those interactions and how the resulting complexes behave as pH and the concentrations of competing ions change.

Table 2 presents selected formation constants for these agents, complementing the amino acid data in Table 1. Comparisons require attention to the metal's oxidation state, the number of ligand molecules involved and the measurement conditions. These constants describe metal binding under specified conditions; they do not, on their own, establish improved plant uptake or fertiliser effectiveness.

Table 2. Selected formation constants of agricultural chelating and complexing agents with nutrient metals.

complexing agent	Metal	log K_1	Conditions	Reference
EDTA	Ca^{2+}	10.75	25°C; ionic strength 0.17 M	Arena *et al.,* (1983)
EDTA	Mg^{2+}	8.93	25°C; ionic strength 0.17 M	Arena *et al.,* (1983)
DTPA	Ca^{2+}	10.7	25°C; 0.1 M KNO_3	Anderegg *et al.,* (2005)
DTPA	Mg^{2+}	9.3	25°C; 0.1 M KNO_3	Anderegg *et al.,* (2005)
DTPA	Mn^{2+}	15.5	25°C; 0.1 M KNO_3	Anderegg *et al.,* (2005)
DTPA	Fe^{2+}	16.0	20°C; 0.1 M $NaNO_3$	Anderegg *et al.,* (2005)

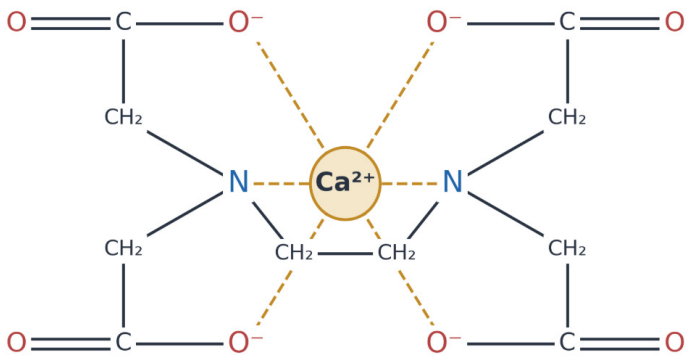
complexing agent	Metal	log K_1	Conditions	Reference
DTPA	Fe^{3+}	27.8	25°C; 0.1 M KNO_3	Anderegg *et al.,* (2005)
DTPA	Zn^{2+}	18.6	20°C; 0.1 M $NaNO_3$	Anderegg *et al.,* (2005)
DTPA	Cu^{2+}	21.5	25°C; 0.1 M $KClO_4$	Anderegg *et al.,* (2005)
o,o-EDDHA	Ca^{2+}	7.29	25°C; 0.1 M NaCl	Yunta *et al.,* (2003a)
o,o-EDDHA	Mg^{2+}	9.76	25°C; 0.1 M NaCl	Yunta *et al.,* (2003a)
o,o-EDDHA	Mn^{2+}	9.57	Ionic strength 0.1 M; temperature and electrolyte to confirm	López-Rayo *et al.,* (2012)
o,o-EDDHA	Fe^{3+}	35.09	25°C; 0.1 M NaCl	Yunta *et al.,* (2003a)
o,o-EDDHA	Cu^{2+}	25.13	25°C; 0.1 M NaCl	Yunta *et al.,* (2003a)
o,p-EDDHA	Ca^{2+}	4.12	25°C; 0.1 M NaCl	Yunta *et al.,* (2003b)
o,p-EDDHA	Mg^{2+}	5.64	25°C; 0.1 M NaCl	Yunta *et al.,* (2003b)
o,p-EDDHA	Mn^{2+}	8.36	Ionic strength 0.1 M; temperature and electrolyte to confirm	López-Rayo *et al.,* (2012)
o,p-EDDHA	Fe^{3+}	28.72	25°C; 0.1 M NaCl	Yunta *et al.,* (2003b)
o,p-EDDHA	Zn^{2+}	12.44	Ionic strength 0.1 M; temperature and electrolyte to confirm	López-Rayo *et al.,* (2012)
o,p-EDDHA	Cu^{2+}	21.74	25°C; 0.1 M NaCl	Yunta *et al.,* (2003b)
Modified lignin derivative	Cu^{2+}	4.07	pH 5; titration calorimetry	Garcia-Valls and Hatton (2003)
Modified lignin derivative	Cu^{2+}	4.96	pH 6; titration calorimetry	Garcia-Valls and Hatton (2003)
Modified lignin derivative	Mg^{2+}	3.11	pH 6; titration calorimetry	Garcia-Valls and Hatton (2003)
Gluconate	Zn^{2+}	1.7	Original measurement conditions to confirm	Reported in Survila *et al.*, (2013)
Gluconate	Cu^{2+}	2.2	Original measurement conditions to confirm	Reported in Survila *et al.*, (2013)

4.1 EDTA.

EDTA (ethylenediaminetetraacetic acid) is a synthetic chelating agent manufactured through industrial chemical synthesis. An established production route uses ethylenediamine, formaldehyde and a cyanide source to produce EDTA salts, which can subsequently be converted into the acid form. EDTA is therefore supplied as a manufactured chemical rather than extracted from protein or plant material.

One EDTA molecule can bind a metal ion through up to six sites: two nitrogen atoms and four oxygen atoms from its carboxylate groups (Figure 2). These multiple attachments allow it to form several chelate rings around the metal. Glycine, by comparison, commonly binds through its amino nitrogen and a carboxyl oxygen. EDTA's multiple binding sites help explain its higher reported formation constant with calcium compared with glycine. This indicates stronger association under the measurement conditions but does not establish greater nutritional effectiveness: calcium must also become available for physiological use, and formation constants alone do not determine its release or utilisation within the plant.

Figure 2. Schematic of calcium chelation by EDTA



The calcium values in Tables 1 and 2 illustrate this difference. Arena *et al.,* (1983) reported a log K_1 of 10.75 for calcium–EDTA at 25°C and an ionic strength of 0.17 M, whereas Ashmead (2012) listed a log K_1 of 1.38 for calcium–glycine. Because these values are base-10 logarithms, each increase of one unit represents a tenfold increase in the formation constant. The difference of 9.37 units therefore corresponds to an approximately 2.3-billion-fold difference between the reported constants.

The reported constants indicate substantially stronger calcium binding by EDTA than by glycine, although the incompletely specified conditions in Ashmead (2012) make this comparison approximate. Strong binding can help maintain a metal in solution, but nutritional effectiveness also requires that the metal becomes available for physiological use. EDTA's strong association therefore raises a question about nutrient release, rather than demonstrating that calcium remains unavailable inside the plant. Amino acid ligands offer a potential additional benefit because they can participate in plant metabolism, alongside their metal-binding role. Whether these properties translate into improved metal release, translocation and nutrition must nevertheless be established through plant experiments rather than inferred from formation constants alone.

4.2 DTPA.

DTPA (diethylenetriaminepentaacetic acid) is a synthetic chelating agent manufactured through industrial chemical synthesis. An established production route uses diethylenetriamine, formaldehyde and sodium cyanide to produce its sodium salt. Like EDTA, DTPA is supplied as a manufactured chemical rather than extracted from proteins or plant material.

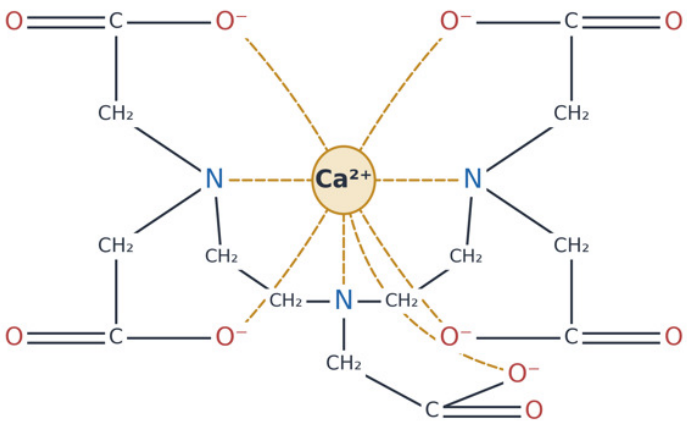
One DTPA molecule contains eight potential metal-binding sites: three nitrogen atoms and five oxygen atoms from its carboxylate groups. These sites allow multiple attachments to the same metal ion, forming several chelate rings (Figure 3). DTPA therefore has more potential binding sites than EDTA, although the number involved depends on the metal and solution conditions. More binding sites do not automatically produce a higher formation constant for every metal (Anderegg *et al.,* 2005).

For calcium, Anderegg *et al.,* (2005) reported a log K_1 of 10.7 at 25°C in 0.1 M KNO_3. This is close to the calcium–EDTA value of 10.75 reported by Arena *et al.,* (1983), indicating similar binding affinity under their respective measurement conditions. The small difference should not be interpreted as an exact ranking because the experimental media differ.

Compared with the calcium–glycine log K_1 of 1.38 listed by Ashmead (2012), the calcium–DTPA value is 9.32 logarithmic units higher. This corresponds to an approximately 2.1-

billion-fold difference between the reported formation constants. As the conditions in Ashmead (2012) were not fully specified, this comparison provides an approximate indication of stronger association rather than a precise measure of performance in a fertiliser or plant.

Figure 3. Schematic of calcium chelation by DTPA



Strong complexation can help maintain a metal in solution, but nutritional effectiveness also requires that the metal becomes available for physiological use. DTPA's high formation constant raises a question about nutrient release. Formation constants describe equilibrium binding rather than the speed of release and cannot alone establish effects on metal translocation or utilisation.

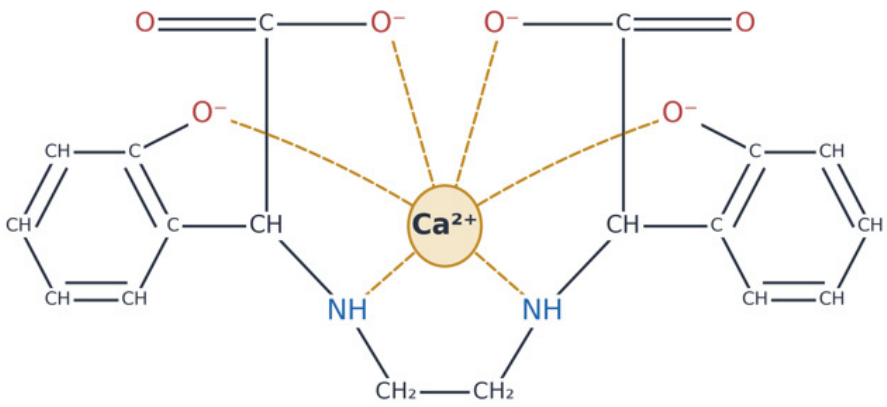
Amino acid ligands offer a potential additional benefit through their participation in plant metabolism. However, whether this produces better nutrient release, translocation or nutrition than DTPA requires direct experimental evidence. Likewise, the nitrogen atoms in DTPA should not be assumed to provide plant-available nitrogen simply because they are present in the molecule.

4.3 EDDHA.

EDDHA (ethylenediamine-N,N'-bis(hydroxyphenylacetic acid)) is a synthetic chelating agent used particularly in iron fertilisers. One manufacturing route combines phenol, ethylenediamine and glyoxylic acid. This reaction can produce different structural forms, known as isomers, together with other reaction products; consequently, commercial EDDHA preparations are not necessarily chemically uniform (Yunta *et al.,* 2003a).

A distinctive feature of EDDHA is its two benzene rings bearing hydroxyl groups. In o,o-EDDHA, these groups are positioned next to the side chains connecting the rings to the rest of the molecule. Their oxygen atoms can participate in metal binding after losing hydrogen ions. Together with two nitrogen atoms and two carboxylate oxygen atoms, they provide six potential binding sites (Figure 4). In o,p-EDDHA, one hydroxyl group occupies a different position, changing the ligand's ability to surround and bind a metal (Yunta *et al.,* 2003a,b).

Figure 4. Schematic of calcium chelation by EDDHA



These structural differences are reflected in Table 2. At 25°C in 0.1 M NaCl, the reported calcium log K_1 values are 7.29 for o,o-EDDHA and 4.12 for o,p-EDDHA. Both are below the calcium values listed for EDTA and DTPA, although the latter were measured in different media. EDDHA therefore does not bind every nutrient more strongly than the other synthetic agents. Its agricultural relevance lies in iron binding: under the same conditions, the reported Fe^{3+} values are 35.09 for o,o-EDDHA and 28.72 for o,p-EDDHA, demonstrating why the isomer composition matters (Yunta *et al.*, 2003a,b).

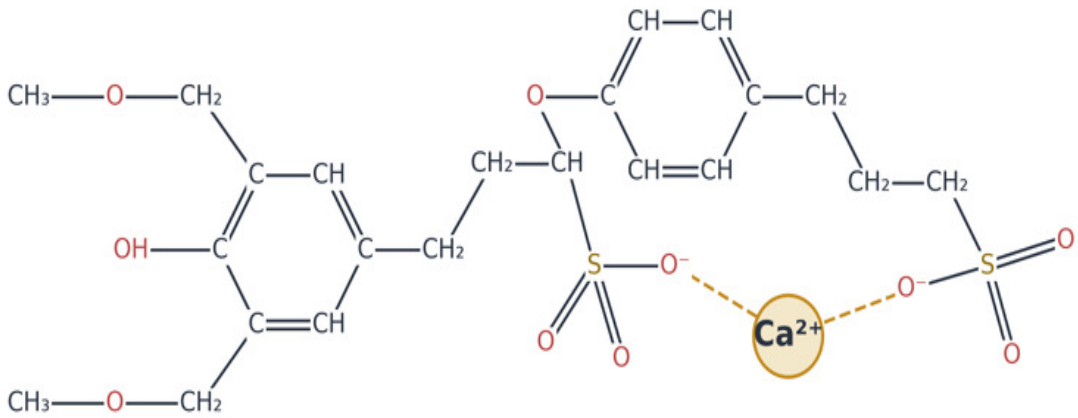
For iron nutrition, strong binding does not necessarily prevent nutrient release. In many non-grass plants, root uptake involves reduction of chelated Fe^{3+} to Fe^{2+}, which can then be released and absorbed. The effectiveness of an iron chelate therefore depends both on maintaining iron in an available form outside the root and on allowing the uptake process to occur. This mechanism concerns iron and should not be assumed to describe calcium release. Likewise, the calcium formation constants do not establish whether calcium–EDDHA enters the plant intact or how it subsequently behaves (Yunta *et al.*, 2003a).

4.4 Lignosulfonates.

Lignosulfonates are water-soluble derivatives of lignin, the structural material that helps strengthen plant cell walls. They are obtained as by-products of sulphite pulping in the paper industry. Unlike the defined molecules discussed above, lignosulfonates comprise mixtures of organic structures with different molecular sizes and functional groups. Their composition therefore varies with the raw material and processing conditions (Villén *et al.,* 2007).

Their oxygen-containing groups can interact with metal ions, while sulfonate groups contribute to water solubility. Metal binding consequently involves a variable organic matrix rather than a uniform arrangement of binding sites (Figure 5). This helps explain why lignosulfonates are generally assessed through their complexing capacity and stability under specified conditions, rather than assigned a single formation constant applicable to every preparation.

Figure 5. Schematic of calcium chelation by Lignosulfonate



Fuentes *et al.,* (2023) reported apparent iron-binding constants of log K = 4.5 for a lignosulfonate–iron preparation (Ls-Nit) and 4.1 for a lignosulfonate–citrate–iron preparation (Ls-Cit), using fluorescence quenching. These values provide an approximate indication of iron-binding stability in the preparations studied and useful context alongside the constants reported for other complexing agents. However, because they depend on the preparation, analytical method and binding model, comparisons with the molecular log K_1 values in Tables 1 and 2 should be considered qualitative rather than quantitative.

Performance also depends on the application environment. Lucena *et al.,* (2010) found that the iron–lignosulfonate preparation tested maintained iron in solution up to approximately pH 7.0–7.5, whereas interactions with soils and soil components substantially altered the amount remaining in solution. Fuentes *et al.,* (2023) further showed that formulation influences the organisation of lignosulfonate-based iron complexes and their interactions with calcium at alkaline pH. Lignosulfonates can therefore serve as metal-complexing agents, but solution stability alone does not establish their nutritional effectiveness after soil application. Their variable composition also means that structural illustrations should depict representative fragments rather than a definitive molecule for the whole class.

The sulphur in lignosulfonate sulfonate groups is organically bound and should be distinguished from sulphate, the principal form absorbed by plant roots. Research on rhizosphere microorganisms demonstrates that microbial desulfonation can mobilise sulphur from organic sulfonates (Schmalenberger *et al.*, 2009). This provides a possible pathway through which lignosulfonate-bound sulphur could contribute to plant nutrition following microbial transformation, but it does not establish the rate or extent of sulphur release from a particular lignosulfonate preparation. Total sulphur content should therefore not be equated with immediately plant-available sulphur; any nutritional contribution requires evidence for the preparation, application rate and growing conditions concerned.

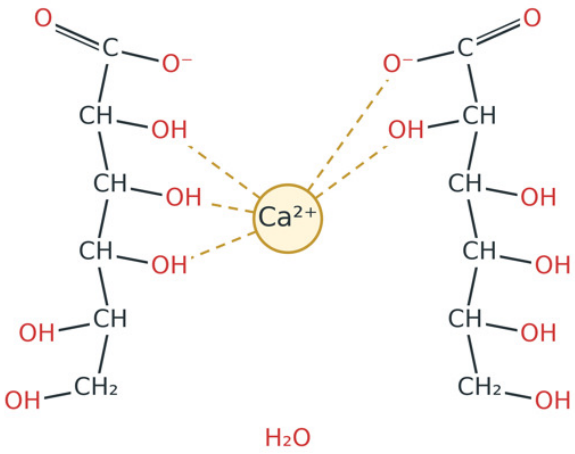
4.5 Gluconates and other organic complexing agents.

Gluconate, the conjugate base of gluconic acid, contains one carboxylate group and five hydroxyl groups that provide potential oxygen donor sites for metal coordination. The groups involved in binding depend on the metal, pH and surrounding chemical environment. Bugris *et al.,* (2018) demonstrated that calcium D-gluconate monohydrate forms a coordination polymer in the crystal, with each calcium ion coordinated to nine oxygen atoms. Five of these contacts originate from the two gluconate ligands within the asymmetric unit, while four involve neighbouring units. Figure 6 illustrates the five contacts within the asymmetric unit rather than the complete polymeric structure.

The constants reported in Table 2 describe specific gluconate-binding equilibria. Survila *et al.,* (2013) compiled log K_1 values of 1.7 for Zn^{2+} and 2.2 for Cu^{2+} for the reaction $M^{2+} + L^{-} \rightleftharpoons$

ML^+. These values provide an indication of relatively weak binding for these particular species compared with the corresponding EDTA and DTPA complexes. However, gluconate can form additional species as conditions change, including hydroxyl-containing complexes, so these constants do not describe its behaviour across the entire pH range. The values were taken from earlier literature rather than newly measured by Survila *et al.,* (2013). Their original measurement conditions remain to be confirmed.

Figure 6. Schematic of the calcium–gluconate chelate.



Agricultural performance also depends on the metal and formulation. Lucena *et al.,* (2010) found that the zinc–gluconate preparation tested maintained approximately all its zinc in solution up to pH 7.5. In contrast, the gluconate-containing iron formulation maintained only approximately 20–40% of its iron in solution over pH 5–11. Because the iron formulation contained other micronutrients, this result should not be treated as an intrinsic limit for every iron–gluconate preparation. Interactions with soils and soil components further altered the amount of metal remaining in solution, demonstrating that stability in a fertiliser solution does not necessarily predict behaviour after soil application.

Other organic complexing agents, including citrate, glucoheptonate and humic substances, also contain oxygen-bearing groups capable of binding metals. Their effectiveness depends on ligand structure, metal identity, pH, competing ions and the composition of the preparation. Gluconates and related agents can consequently help maintain nutrients in solution under suitable conditions, but their suitability should be evaluated for the intended

nutrient and application environment. Complex formation alone does not establish intact uptake of the complex or improved nutrient delivery to the plant.

5. Behaviour in soil and nutrient solutions.

The composition of an amino acid–mineral formulation at manufacture does not necessarily remain unchanged after application. Dilution and contact with irrigation water, other fertilisers or soil introduce a different chemical environment. The resulting distribution between complexed and uncomplexed metal depends on the final concentrations of the ingredients and the surrounding solution, rather than solely on the formation constants discussed in Section 3.

In nutrient solutions, the relevant conditions are those of the final mixture supplied to the crop. Alongside pH, the concentrations of other metals and dissolved ligands influence which complexes can form. Phosphate, carbonate and hydroxide can also favour precipitation when sufficient uncomplexed metal is present. Maintaining a nutrient in solution therefore depends on the balance between complex formation and competing reactions. Lucena et al., (2010) found that the amino acid–iron preparation tested retained little iron in solution above pH 3, highlighting a formulation-specific limitation rather than a general property of all amino acid–iron complexes. Compatibility should consequently be assessed after mixing and dilution, rather than inferred from the stability of the original product alone.

Soil introduces additional interactions with mineral surfaces, organic matter and microorganisms. Metal nutrients may be retained by adsorption or incorporated into poorly soluble phases, while ligands can interact with soil surfaces or naturally occurring metals.

For amino acid ligands, biological turnover is an additional consideration. Soil microorganisms can consume amino acids, while their retention and movement vary with molecular charge and soil properties. Näsholm *et al.,* (2009) described how amino acid concentrations near roots are shaped by microbial activity, soil retention and transport, and can differ from concentrations in the surrounding bulk soil. This evidence concerns amino acids generally; it does not establish identical turnover rates for their metal complexes.

Nevertheless, microbial consumption of the available amino acid pool could alter the conditions supporting metal binding. Biodegradability should therefore be considered alongside persistence when evaluating an amino acid–mineral formulation.

The practical behaviour of these formulations must consequently be assessed under the intended application conditions. In nutrient solutions, useful measurements include changes in pH, precipitation and the proportion of metal remaining dissolved after mixing and storage. In soil, retention, movement and biological turnover also become relevant. Dissolved metal, amino-acid-bound metal and plant-available metal are distinct measurements and should not be treated as interchangeable. These environmental processes determine the forms that reach the root surface; the mechanisms of nutrient release and subsequent uptake are considered in the following sections.

6. Dissociation and nutrient release.

The nutritional value of a metal complex depends on both maintaining the nutrient in an accessible form before uptake and allowing its subsequent release for physiological use. The strongest binding is therefore not necessarily the most beneficial. Amino acids offer a potentially useful combination: their metal-binding properties vary with their structure, while the ligand itself can contribute to plant metabolism after absorption and utilisation.

Release from an amino acid–mineral complex can occur through dissociation or transfer of the metal to another ligand. When two amino acids bind one metal, loss of the first leaves a metal–amino acid complex; complete dissociation requires loss of the remaining ligand. Removal of released metal through uptake or another reaction can favour further dissociation. The extent of release depends on the surrounding concentrations and competing reactions, while its speed depends on the kinetics of the complex. Consequently, neither strong binding nor moderate binding alone establishes how rapidly a nutrient becomes available.

Compared with EDTA and DTPA, amino acid ligands offer an additional potential nutritional contribution. Plants possess mechanisms for absorbing amino acids and incorporating their carbon and nitrogen into metabolism (Näsholm *et al.,* 2009). Where an applied amino acid

becomes available for these processes, it can serve a purpose beyond metal binding. This distinguishes amino acids from ligands whose presence does not itself establish a contribution to plant nutrition. However, the nutritional importance of the amino acid depends on its identity, the amount absorbed and the plant's requirements; it should not be inferred simply from its inclusion in a fertiliser.

Calcium illustrates the distinction between binding strength and nutritional function. EDTA binds calcium substantially more strongly than glycine under the reported measurement conditions in Tables 1 and 2. This stronger association can help retain calcium in a complex but does not establish superior delivery to physiological sites. Conversely, weaker calcium–glycine binding may permit release under suitable conditions. The potential advantage of an amino acid formulation therefore lies in achieving adequate calcium availability together with a metabolically useful ligand, rather than assuming that either maximum binding strength or minimum binding strength is preferable.

Metabolism of the amino acid could also influence metal release if it removes available ligand or changes the binding molecule. Nevertheless, the established utilisation of free amino acids does not demonstrate that an intact metal complex is absorbed or that its ligand is immediately metabolised. These are separate steps that require evidence for the preparation. The same distinction applies to EDTA and lignosulfonate formulations: their formation constants and external solution behaviour cannot, by themselves, establish the fate of their complexes inside the plant.

Amino acid–mineral formulations consequently offer the prospect of combining mineral delivery with a useful organic nutrient. Their advantage is most convincingly demonstrated when appropriate binding and release are accompanied by improved mineral nutrition and utilisation of the amino acid component. This combined function provides a strong rationale for their agricultural use, while comparisons with conventional agents must account for the nutrient, formulation and application conditions. The following section examines how uptake and subsequent processing determine whether this potential is realised.

7. Uptake and utilisation of complexed mineral nutrients.

Following foliar application, nutrients may penetrate through aqueous pathways in the cuticle or through stomatal pathways, depending on the leaf and formulation. Neither route guarantees entry of the intact complex. After penetration, nutrients reach the apoplast, comprising cell walls and extracellular spaces. Entry into the symplast, the interiors of living cells, requires crossing a plasma membrane. Table 3 summarises this process.

Table 3. Uptake, movement and metal release from agricultural complexing agents.

Agent	Entry and movement	Metal release and subsequent utilisation
Amino acids	Foliar delivery is demonstrated. Rezende *et al.,* (2025) detected metals in both apoplast and symplast after amino acid complex application, predominantly in the apoplast. The study did not distinguish cuticular from stomatal entry or establish whether the complexes remained intact.	Dissociation and exchange with plant ligands are possible release mechanisms. Changes in pH can alter binding, but the study did not identify the release site, rate or a specific enzyme. Once separately available, the amino acid can enter metabolism.
EDTA	Can deliver nutrients through roots and leaves. Root-supplied metal need not retain EDTA during subsequent transport: Montanha *et al.,* (2020) identified association with plant ligands instead.	The original binding arrangement changes before long-distance transport, although the exact exchange site was unresolved. For iron, root-surface ferric-chelate reductase reduces complexed Fe^{3+} to Fe^{2+}, making iron available for uptake. This changes the metal's oxidation state rather than destroying the ligand (Robinson *et al*., 1999).
DTPA	Maintains an external supply of dissolved metal. A complete pathway showing intact passage through the leaf surface and into the symplast is not established in the evidence considered.	Dissociation, exchange or, for iron, reduction can potentially provide access to the metal. Their relative contributions and intracellular locations require direct evidence.
EDDHA	Root uptake and movement of some intact Fe–EDDHA in xylem sap are demonstrated (Orera *et al.*, 2010). Xylem detection does not establish entry into the cytoplasm.	Iron acquisition can involve root-surface reduction. The intact fraction detected in xylem shows that release is not obligatory before vascular transport; its subsequent release site was not identified.

Lignosulfonates	Root and foliar nutrient delivery have been demonstrated. Uptake of the metal does not establish entry of the whole lignosulfonate molecule.	Acquisition depends on the preparation. Exchange and iron-acquisition processes may contribute, but a general intracellular polymer-cleaving enzyme or release compartment has not been demonstrated.
Gluconates	Foliar preparations have been investigated, but intact-complex passage into the symplast remains unresolved in the evidence considered.	Dissociation and ligand exchange are possible mechanisms. A specific intracellular release site, enzyme or comparative release rate has not been established.

Amino acids combine metal binding with a ligand that can itself participate in plant metabolism. Rezende *et al.,* (2025) also demonstrated improved foliar metal transport under low humidity and less visible injury than sulphate treatments. These are specific delivery advantages, although the study did not compare synthetic chelators or measure intracellular release speed.

8. Conclusion.

Amino acids provide a flexible group of metal-binding ligands whose agricultural value can extend beyond complexation. Their structures offer different binding affinities, and available amino acids can participate in plant metabolism. Experimental evidence supports effective nutrient delivery and, under particular experimental conditions, improved transport. These benefits provide a sound rationale for their use in nutrient formulations.

Selection nevertheless depends on the nutrient, formulation and application environment. EDTA, DTPA and EDDHA can provide strong protection of dissolved metals, while lignosulfonates and gluconates offer other formulation options. Amino acid complexation does not guarantee stability in soil or faster intracellular release. The useful comparison is whether an agent maintains nutrient availability during delivery and supports acquisition and physiological utilisation under the intended conditions. Amino acids are particularly attractive when those functions are accompanied by utilisation of the ligand itself.

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