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Copper(II) Complexes of the Imidazolinone Herbicide Imazapyr

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The copper(II) complexes formed by the imidazolinone herbicide imazapyr [(±)-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid] were studied in aqueous solution by potentiometric and spectroscopic techniques. Imazapyr acts as a chelating molecule and is effective over a wide pH range. The chelating set active in acidic media involves rather weak donors, namely the pyridine and imidazole nitrogens. In neutral media, the lactam site of the imidazolinone ring deprotonates and the ligand takes advantage of a rather basic nitrogen atom, which, assisted by the pyridine donor, yields stable complexes with five-coordination at the metal ion.

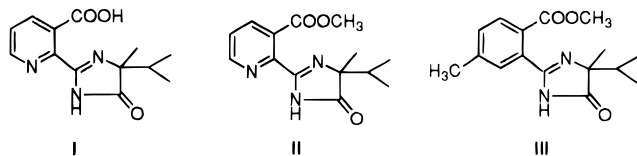
Keywords: Imazapyr; 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid; copper(II) complexes

INTRODUCTION

Pesticides may have a significant impact on metal biocycles in soil. In particular, the interaction of pesticides with clay components may promote the desorption of metal ions from the colloidal phase, surface precipitation of insoluble complexes, sorption of the ligand itself, etc. Carboxylic herbicides such as Fluazifop [(±)-2-[4-[(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid] and diclofop [(±)-2-[4-(2,4-dichlorophenoxy)phenoxy]propanoic acid] promote metal ion desorption by forming neutral complexes or ion pairs that are soluble in the aqueous phase (Micera et al., 1988; Pusino et al., 1989). In contrast, their estereal derivatives are ineffective in metal mobilization and act as hydrophobic screens that hinder the cation exchange.

Metal ion immobilization in clays is observed upon adsorption of acifluorfen [5-[2-chloro-4-(trifluoromethyl)-2-phenoxy]-2-nitrobenzoic acid], a herbicide applied in the field as the sodium salt (Kozłowski et al., 1990; Pusino et al., 1991). In this case, the low solubility of the formed complexes is the driving force of the whole process that likely produces inactivation of the herbicide, the activity of which is critically regulated by the concentration in soil solution.

Imidazolinone molecules, introduced by American Cyanamid Company, are one of the most active classes of herbicides. To understand their metal binding properties, we investigated the copper(II) complexes formed in aqueous solution by a representative member of the class, imazapyr (**I**, Imz).



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Table 1. Stability Constants (log β) of the Proton and Cu(II) Complexes at 25 °C and 0.1 M (KNO₃) Ionic Strength

species	Imz	ImzOMe	ImzbOMe
H ₃ A	16.29(1)		
H ₂ A	14.41(1)	11.76(1)	13.63(1)
HA	10.81(1)	9.74(1)	10.39(1)
pK _{COOH}	3.60		
pK _{NH(im)}	1.88	2.02	3.24
pK _{NH(lact)}	10.81	9.74	10.39
CuAH	14.8(1)		
CuA ₂ H ₂	29.52(4)		
CuA ₂ H	23.20(4)		
CuA ₂	15.99(4)		

MATERIALS AND METHODS

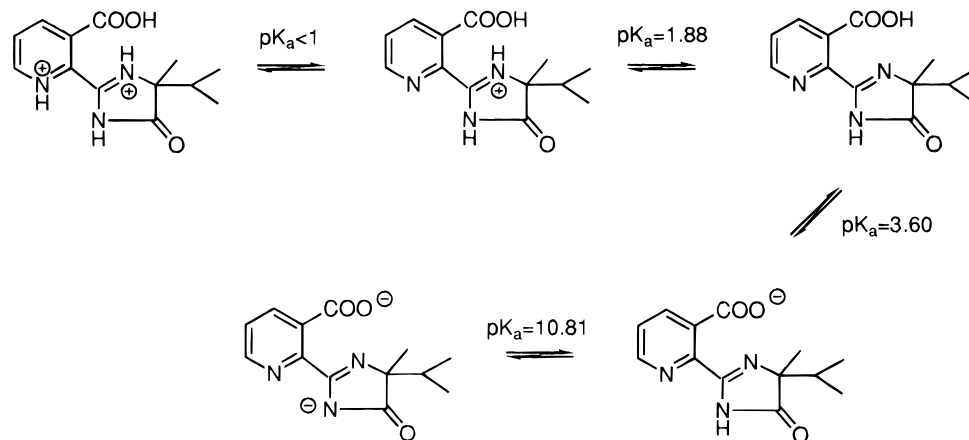
Ligands. Imazapyr and imazamethabenz-methyl (**III**, ImzbOMe) were kindly supplied by American Cyanamid Company, Princeton, NJ. The methyl ester of imazapyr (**II**, ImzOMe) was synthesized by dissolving the acid in dry methanolic H₂SO₄ solution and heating at reflux for 2 h. The reaction mixture was washed with an aqueous NaHCO₃ solution, and the organic layer was dried with anhydrous Na₂SO₄ and evaporating under reduced pressure.

Potentiometric Measurements. The acidity and stability constants were calculated from pH titration data obtained at 25 °C, with a total volume of 2.0 mL. Alkali was added from a 0.1-mL micrometer syringe calibrated by both weight titration and titration of standard materials. Experimental details were as follows: ligand concentration, 3×10^{-3} M; metal-to-ligand molar ratios, 1:1, 1:2, 1:3, and 1:4; and ionic strength, 0.1 M KNO₃. The experimental method was as follows: pH-metric titrations on a Molspin pH-meter system with a Russell micro combined glass/calomel electrode calibrated in concentration with HNO₃ (Irving et al., 1967); number of titrations, four; and method of calculations, SUPERQUAD program (Gans et al., 1985). The samples were titrated from pH 2.2 to 11.0.

As usual, the stabilities of the metal complexes are reported as the logarithms of the overall formation constants $\beta_{pqr} = [M_p A_q H_r] / [M]^p [A]^q [H]^r$, where M stands for the metal ion, H the proton, and A the fully deprotonated ligand (Table 1). Overall formation constants may also be used to describe the protolytic equilibria for the ligands, which are assumed to be proton complexes. The standard deviations (σ values) quoted were computed by SUPERQUAD and refer to random errors only. They σ values give however, a good indication of the importance of the particular species in the equilibrium.

Spectroscopic Measurements. Electron paramagnetic resonance (EPR) spectra were recorded on a Varian E9

Scheme 1



spectrometer at the X-band frequency (9.15 GHz) at 140 K. Absorption spectra were recorded on a Beckman Acta IV spectrophotometer.

RESULTS AND DISCUSSION

Ligand. Careful evaluation of the titration curves of the imazapyr ligand allows calculation of the pK_a values of three proton dissociation steps (1.88, 3.60, and 10.81), so the ligand is denoted as H_3A . The values are in quite good agreement with those (adjusted to zero ionic strength) of 1.81, 3.64, and 11.34 reported in the literature (Chamberlain et al., 1995). The unambiguous assignment of the deprotonation processes is made possible by comparison of related compounds; namely, the methyl ester of imazapyr and the *para* isomer of imazamethabenz-methyl, which is also a methyl ester. Titration data show two ionization processes with pK_a values of 2.02 and 9.74 for ImzOMe, and two ionization processes, with pK_a values of 3.24 and 10.39 for the *para* form of imazamethabenz-methyl, which lacks the carboxylic group and the pyridine nitrogen atom.

The data summarized in Table 1 indicate, as expected, that the pyridine nitrogen of the imazapyr molecule has very low basicity, the pK_a value of the corresponding protonated form being not measurable (<1). The pK_a values of 1.88 and 3.60 may be assigned to the deprotonation of the imidazole nitrogen and the carboxylic group, respectively. The dissociation process that occurs with $pK_a = 10.81$, is thus distinctive of the deprotonation of the lactam group, as shown in Scheme 1. The data can be related to those of 2,2'-bipyridine ($pK_{a1} = -0.2$, $pK_{a2} = 4.44$), 2-(2-pyridyl)imidazole ($pK_{a1} = -0.7$, $pK_{a2} = 5.47$), 4-(2-pyridyl)imidazole ($pK_{a1} = 1.3$, $pK_{a2} = 5.49$), and 1,10-phenanthroline ($pK_{a1} = -1.6$, $pK_{a2} = 4.95$) reported by Eilbeck and Holmes (1967). From such a comparison it is evident that pK_a values are critically affected by various factors, including the charge repulsion in the protonated forms, resonance effects, etc. The pyridinic substitution in the 2 position of the imidazole ring lowers the basicity of the N(1) atom as an effect of conjugation [e.g., the pK_a value of the protonated form decreases from 7.03 in imidazole (Martell and Smith, 1986) down to 5.49 in 2-(2-pyridyl)imidazole (Eilbeck and Holmes, 1967)]. An effect of the presence of a carbonyl group and the pyridinic substitution in the imidazole ring of imazapyr is that the acidity of the ring nitrogens is greatly increased. In particular, the pK_a value of the 'imidazole' nitrogen decreases down to ~ 2 . On the other hand, the ionization of the lactam group occurs with a pK_a of 10.8 (cf the pK_a value of ~ 15

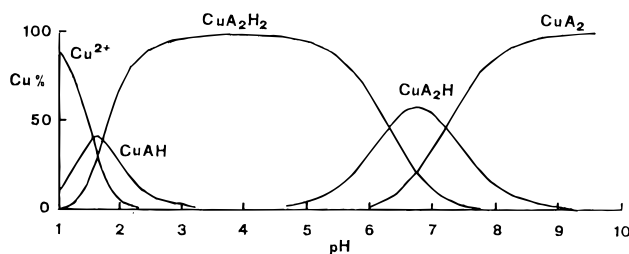


Figure 1. Speciation curves for complexes formed in the Cu(II)-Imz system at Cu(II) concentration of 1×10^{-3} M and metal-to-ligand molar ratio 1:3.

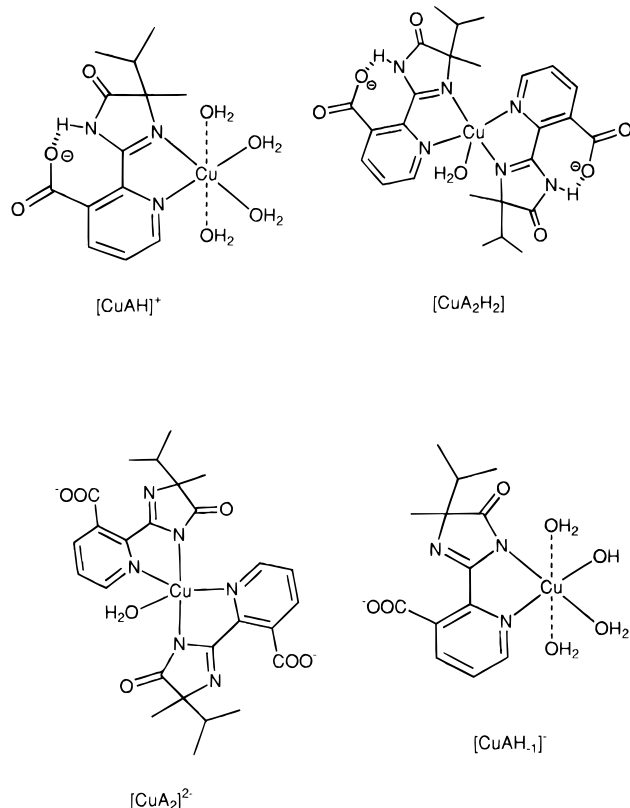
for the pyrrolic group of imidazole), which makes available a strong coordination site, analogous to that of peptide molecules, over the measurable pH range.

Cu(II)-Imz System. Potentiometric data for the Cu(II)-Imz system (Table 1 and Figure 1) were fitted by the CuAH, CuA_2H_2 , CuA_2H , and CuA_2 species (charges are omitted for ease of notation). In the first two species, the ligand molecules have undergone dissociation at the carboxylic and imidazole groups. The involvement of both of these groups in the coordination to a single metal ion is unlikely (and ruled out by spectral measurements) because of the instability of a seven-membered chelated ring. Nevertheless, the metal binding to one of these sites promotes the deprotonation of the other one. The dissociation of the imidazolinone rings with loss of the lactam protons occurs sequentially to yield first an intermediate CuA_2H and then a CuA_2 complex, with pK_a values of 6.32 and 7.21, respectively. The much easier deprotonation, as compared with the free ligand, proves that lactam nitrogens take part in coordination and, as more efficient donors, replace imidazole nitrogens.

The values of the equilibrium constants for the reactions $Cu^{2+} + HA^- \rightleftharpoons CuAH^+$ ($10^{3.99}$) and $Cu^{2+} + 2 HA^- \rightleftharpoons CuA_2H_2$ ($10^{7.90}$) are significantly lower if compared with the analogous constants for the 2,2'-bipyridine complex ($10^{8.11}$ and $10^{13.66}$; Arena et al., 1976; Bonomo et al., 1979), and this is an indication of the rather weak basic properties of the involved donors. On the other hand, the formation constant for CuA_2 is $10^{15.99}$, which is greater by more than two orders of magnitude than those of the bis complexes formed by 2,2'-bipyridine and 2-(2-pyridyl)imidazole ($10^{13.64}$; Martell and Smith, 1986). This difference substantiates that a noticeably more stable chelated complex is formed upon replacement of imidazole by the deprotonated lactam donors in metal coordination.

The coordination pattern was checked by spectral

Scheme 2



measurements. At a ligand molar excess of 2:1 and a Cu(II) concentration of 5×10^{-3} M, already in rather acidic solution (pH ~ 1), EPR spectra indicate, besides the Cu hyperfine resonances of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ($g_{\parallel} = 2.411$ and $A_{\parallel} = 137 \times 10^{-4} \text{ cm}^{-1}$), resonances indicative of a first complex with $g_{\parallel} = 2.310$ and $A_{\parallel} = 165 \times 10^{-4} \text{ cm}^{-1}$. Such parameters are very close to those of the 1:1 complex of 2,2'-bipyridine (bipy) in aqueous solution, for which g_{\parallel} and A_{\parallel} values in the ranges 2.305–2.315 and $164\text{--}166 \times 10^{-4} \text{ cm}^{-1}$, respectively, were measured (Noack and Gordon, 1968; Walker and Sigel, 1972; Marov et al., 1978). The results confirm that the coordination in the Cu(II)-Imz complex system starts with formation of a CuAH species where the metal ion behaves as a bipy-like chelator, coordinating through pyridine and imidazole nitrogens (Scheme 2). Above pH 3, the CuA_2H_2 complex, with two ligands adopting this bipy-like mode, is revealed by the hyperfine broadening in the parallel region. Upon deprotonation of the lactam group (pH > 7.5) and formation of CuA_2 , the spectra are much broader and exhibit distinct components at $g \sim 2$, indicating a nontetragonal geometry at the copper ion. In very basic solution (pH > 11.5) a further single species is detected ($g_{\parallel} = 2.237$ and $A_{\parallel} = 194 \times 10^{-4} \text{ cm}^{-1}$), which exhibits normal tetragonal character and is assigned as the hydrolyzed complex $\text{CuA}(\text{OH})$ or CuAH_{-1} . Actually, these parameters are comparable to those of $[\text{Cu}(\text{bipy})\text{OH}]^+$ ($g_{\parallel} = 2.233$ and $A_{\parallel} = 197 \times 10^{-4} \text{ cm}^{-1}$). The monochelated nature of the species is confirmed by the EPR line width due to unresolved ^{14}N coupling. From the EPR parameters of Cu(II)-Imz and Cu(II)-bipy systems listed in Table 2, it can be seen that the band linewidth increases with increasing number of coordinated nitrogens and, therefore, is a reliable criterion for assigning the donor set.

To obtain more detailed information on the complex species formed in the pH range 3–11, solutions with greater ligand excess were examined. For instance,

Table 2. EPR Parameters for bipy- and Imz-Cu(II) Complexes with $d_{x^2-y^2}$ Ground State^a

species	g_{\parallel}	$A_{\parallel} (10^{-4} \text{ cm}^{-1})$	$\Delta H_{\parallel} (\text{mT})$
$[\text{Cu}(\text{bipy})]^{2+}$	2.307	170	3.9
$[\text{Cu}(\text{bipy})_2]^{2+}$	2.263	162	6.5
$[\text{Cu}(\text{bipy})\text{OH}]^+$	2.233	197	4.1
CuAH	2.310	165	4.1
CuA_2H_2	2.242	188	6.4
CuAH_{-1}	2.237	194	4.3

^a Linewidth of the low field parallel hyperfine resonance.

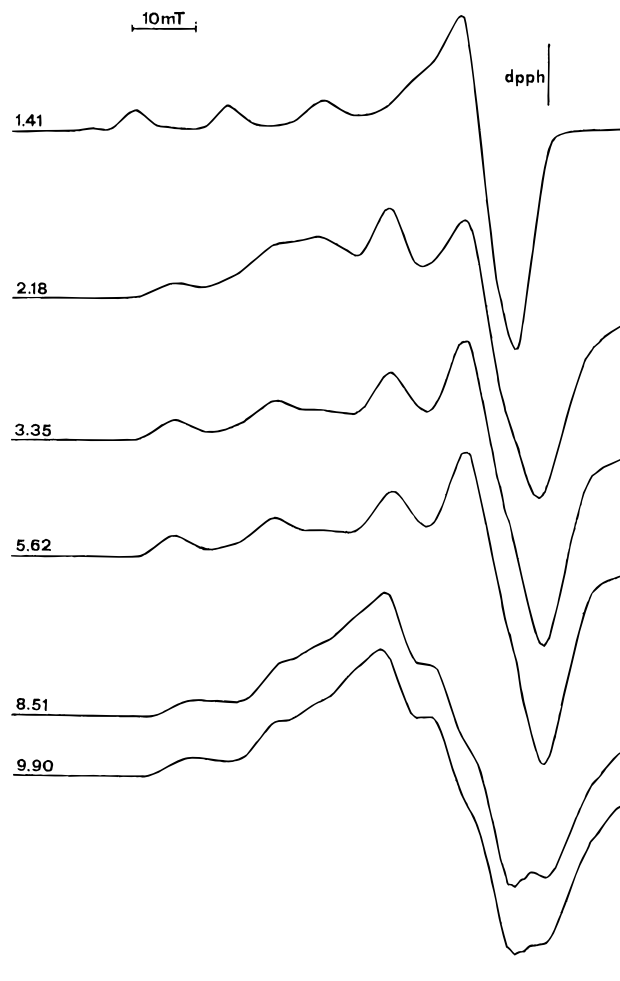


Figure 2. X-band EPR spectra recorded on the Cu(II)-Imz system, at Cu(II) concentration of 5×10^{-3} M and metal to ligand molar ratio 1:10, with varying pH.

spectra collected at 10:1 ligand to metal molar ratio (Figure 2) confirm the CuAH complex at very low pH and its complete transformation into CuA_2H_2 predominating from pH 2 to 6 and characterized by the data set $g_{\parallel} = 2.242$ and $A_{\parallel} = 188 \times 10^{-4} \text{ cm}^{-1}$. The parameters are significantly different from those of the bipy species ($g_{\parallel} = 2.26\text{--}2.28$, A_{\parallel} ca. $162 \times 10^{-4} \text{ cm}^{-1}$, and $g_{\parallel}/A_{\parallel} \approx 140 \text{ cm}$; see Noack and Gordon, 1968; Walker and Sigel, 1972; Marov et al., 1978), indicating a different symmetry at the metal ion. Actually, steric reasons, particularly the repulsion between 3 and 3' protons, hinder the coplanarity of ligand molecules in the bis complexes of bipy (McKenzie, 1971). According to Sigel (1972), electronic effects could contribute to such a deviation. In our case, a *cis* arrangement for the ligands can be excluded by spectral data indicative of a $d_{x^2-y^2}$ instead of d_{z^2} ground state (Hathaway, 1984). Comparison with a nearly planar CuN_4 chromophore of the bis-chelated complex of 2-aminomethylpyridine

Table 3. Electronic Absorption Maxima of the Cu(II) Complexes of Imz

species	λ_{\max} (nm)	ϵ^a ($M^{-1} \text{ cm}^{-1}$)
CuAH	735	52
CuA ₂ H ₂	704	78
CuA ₂	658	100
CuAH ₋₁	560	63

^a ϵ is the molar extinction coefficient measured at the maximum extent of formation of the species and referred to the total metal concentration.

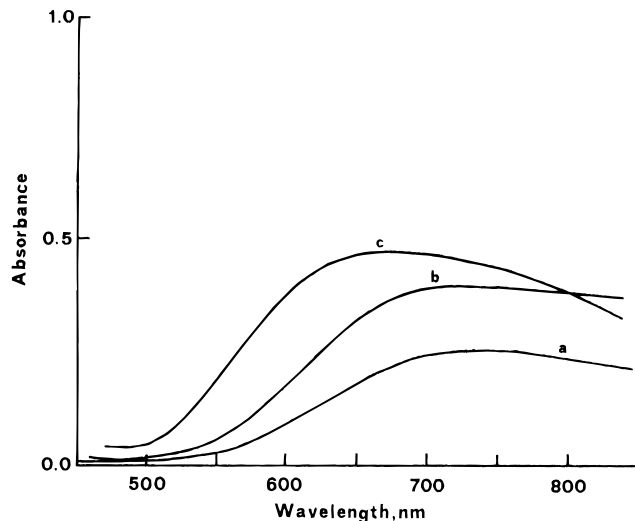


Figure 3. Electronic absorption spectra recorded on the Cu(II)-Imz system, at Cu(II) concentration of 5×10^{-3} M and metal to ligand molar ratio 1:10, with varying pH (a, 1.40; b, 3.50; c, 9.90).

(Várnagy et al., 1994), characterized by $g_{\parallel} = 2.220$ and $A_{\parallel} = 198 \times 10^{-4} \text{ cm}^{-1}$ ($g_{\parallel}/A_{\parallel} = 112 \text{ cm}$), shows that tetrahedral distortion occurs in CuA₂H₂ ($g_{\parallel}/A_{\parallel} = 119 \text{ cm}$), although to a lower extent than in [Cu(bipy)₂]²⁺. The tetrahedral type of distortion is confirmed by the absorption spectrum, particularly by the large extinction coefficient (Table 3 and Figure 3). Unlike bipy, 2,2'-bi-imidazole can form bis chelated complexes with nearly coplanar ligands [e.g., in diaquabis(2,2'-bi-imidazole)-nickel(II); Mighell et al., 1969]. Therefore, it is likely that the coupling of a pyridinic to an imidazole ring allows for the formation of an imazapyr-Cu(II) complex in which the geometric distortion at the metal ion is partly relaxed.

An examination of the spectra in Figure 2 shows that the deprotonation of lactam groups leads to EPR spectra atypical for Cu(II) with tetragonal or tetrahedral distortion. The spectral features are those expected for five-coordinate complexes with a geometry intermediate between the limit forms of the square pyramid and trigonal bipyramid. Even if a rather precise analysis is not allowed by X-band frequency spectra, it is possible to extract approximate magnetic parameters for the orthorhombic spectrum of CuA₂ ($g_3 = 2.265$, $g_2 = 2.170$; $A_3 = 138 \times 10^{-4} \text{ cm}^{-1}$, $A_2 = 89 \times 10^{-4} \text{ cm}^{-1}$; $g_1 \approx 2.01$). The spectrum of the intermediate CuA₂H species cannot be distinctly observed because of the coexistence of CuA₂H₂ and CuA₂.

According to the diagrams presented in the literature (Bencini et al., 1978), the EPR data set of CuA₂ is in accordance with a five-coordination and a geometry close to the trigonal bipyramid. Therefore, the deprotonation changes not only the binding mode of the ligand, which adopts deprotonated amide instead of imidazole nitrogen for metal binding, but also the metal geometry that

transforms from tetragonal, with tetrahedral distortion, to five-coordinate essentially of the trigonal bipyramid type. This metal geometry is in accord with a chelated mode of the ligand via coordination of the pyridine and deprotonated amide nitrogens. The fifth position is occupied by a molecule of solvent (Scheme 2).

CONCLUSIONS

The imazapyr molecule exhibits a quite interesting and efficient metal binding behavior. The lactam site of the imidazolinone ring is a potential target for metal ions in neutral media and, through the assistance of the pyridine nitrogen, can give rise to very stable chelated species. On the other hand, the pair of pyridine and imidazole nitrogens can bind the metal ion even in rather acidic solution, yielding neutral species that can likely promote the desorption of divalent metal ions from clay surfaces. Therefore, it is expected that the metal-chelating properties may play a significant role in the impact mechanisms of this herbicide on the environment. Moreover, the free carboxylate groups could interact with soil colloidal components (e.g., hydrous oxides) effective in anion binding or ligand exchange processes, thereby promoting the surface anchoring of the complex species.

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