

Metal Complexes of Glufosinate

Christa Ambrose and Patrick E. Hoggard*

Glufosinate acts as a tridentate or tetradentate ligand at near-neutral pH to form complexes with many of the metal ions normally found in groundwater, including Mg^{2+} , Cu^{2+} , Ni^{2+} , Fe^{2+} , and Fe^{3+} . Coordination of the amine, carboxylate, and phosphonate groups to several metal ions was established by IR and UV-visible spectroscopy. The glufosinate complexes are more soluble in water than their glyphosate analogues.

Recently we investigated the tendency of some herbicides to chelate to metal ions (Heaster and Hoggard, 1988; Subramaniam and Hoggard, 1988). Molecules with amine, pyridine, carboxylate, or phosphonate groups are potentially strong complexing agents, and picloram (pyridine, carboxylate) and glyphosate (amine, carboxylate, phosphonate) do form such complexes readily. A potentially important advantage of complexation is that when the complex formed is neutral, it is often also insoluble in water. Both picloram and glyphosate form insoluble complexes with ferrous or ferric ions, and other ions as well, that could provide a natural mechanism for their removal from groundwater or other contaminated waters (Heaster and Hoggard, 1988; Subramaniam and Hoggard, 1988).

Glufosinate (2-amino-4-[(hydroxymethyl)phosphinyl]butanoic acid) is structurally similar to glyphosate (Minowa et al., 1983). A phosphinate group replaces the phosphonate of glyphosate. It is marketed as a postemergent foliar herbicide (Hoechst; trade names Basta, Rubout, and Total) having both contact and systemic activities on grasses and broadleaves (Hopkins and Thomson, 1985). Its mammalian toxicity is quite low because it apparently cannot cross the blood-brain barrier (Kishore and Shah, 1988).

Phosphinate groups are known to form strong coordination complexes with several metal ions, among them Mn^{2+} , Co^{2+} , and Pb^{2+} (Colomarino et al., 1976; Betz and Bino, 1988). Consequently, we have explored the ability of glufosinate to coordinate to several metal ions commonly present in groundwater, and we assess here the implications of such complexation for groundwater contamination.

EXPERIMENTAL SECTION

Glufosinate (free acid = H_2gluf) was provided as the monoammonium salt, NH_4gluf , by Farbwerke Hoechst GmbH, Frankfurt am Main, West Germany.

[Mg(gluf)] \cdot 4H₂O \cdot 5CH₃OH. Glufosinate (1.97 g, 0.010 mol) and KOH (1.12 g, 0.020 mol) were dissolved in 25 mL of water, and the solution was heated for 30 min. $MgCl_2\cdot 6H_2O$ (2.03 g, 0.010 mol) in 25 mL of CH_3OH was added. The solution was kept for several days at room temperature. During this time a white solid was precipitated, which was collected, washed with CH_3OH , and air-dried. The compound was only slightly soluble in cold water but dissolved slowly in warm water. It had a molar conductivity of $178 \Omega^{-1} cm^2 mol^{-1}$, indicating that extensive dissociation takes place in solution. Anal. Calcd for $Mg(C_5H_{10}NO_4P)_2\cdot 4H_2O\cdot 5CH_3OH$: C, 22.66; H, 6.92; N, 4.81. Found: C, 22.42; H, 7.37; N, 5.08.

[Cu(gluf)]. The same procedure as for the magnesium complex was used, starting with 3.70 g (0.010 mol) of $Cu(ClO_4)_2$. The blue crystalline product was only slightly soluble in cold water but dissolved slowly in warm water. It had a molar conductivity of

$10.0 \Omega^{-1} cm^2 mol^{-1}$, indicating a neutral compound with some degree of dissociation. Energy-dispersive X-ray fluorescence (EDXRF) analysis showed the presence of Cu and P, but no Cl. A powder X-ray diffraction spectrum confirmed the crystallinity of the compound. Anal. Calcd for $Cu(C_5H_{10}NO_4P)_2$: C, 24.75; H, 4.15; N, 5.77. Found: C, 24.47; H, 4.35; N, 5.35.

[Ni(gluf)(H₂O)]₂ \cdot H₂O. Again, the same procedure as for the magnesium complex was used, starting with 3.66 g (0.010 mol) of $Ni(ClO_4)_2\cdot 6H_2O$. Crystallization did not occur spontaneously, but a pale blue solid separated when CH_3CN was added. The solid was soluble in water and had a molar conductivity of $0.38 \Omega^{-1} cm^2 mol^{-1}$, indicating a neutral complex not subject to dissociation. EDXRF analysis showed the presence of Ni and P, but no Cl. Anal. Calcd for $Ni_2(C_5H_{10}NO_4P)_2\cdot 3H_2O$: C, 22.69; H, 4.95; N, 5.29. Found: C, 22.76; H, 5.53; N, 5.24.

K_{0.5}(NH₄)_{0.5}[Cr(gluf)₂] \cdot 3H₂O. Glufosinate (1.97 g, 0.010 mol) and $Cr(ClO_4)_3\cdot 6H_2O$ (2.29 g, 0.0050 mol) were dissolved in 50 mL of CH_3OH , and the solution was refluxed for 1 h. KOH (1.12 g, 0.020 mol) was added and the reflux continued for 1 h. The solution was cooled, and the precipitated $KClO_4$ was filtered off. Upon addition of CH_3CN a violet solid separated out which was soluble in water. The molar conductance in aqueous solution of this material was $94 \Omega^{-1} cm^2 mol^{-1}$, which is consistent with a 1:1 electrolyte (Meites and Thomas, 1958). The complex was eluted from a Dowex 1-X8 anion-exchange column as a single band with 0.3 M NaCl as the eluent, characteristic of a uninegative complex. EDXRF analysis showed the presence of Cr, K, and P, but no Cl. Anal. Calcd for $K_{0.5}(NH_4)_{0.5}[Cr(C_5H_{10}NO_4P)_2]\cdot 3H_2O$: C, 24.36; H, 5.72; N, 7.10. Found: C, 24.79; H, 5.89; N, 7.04.

K[Co(gluf)₂]. A procedure similar to that for the chromium complex was followed, starting with 1.83 g (0.0050 mol) of $Co(ClO_4)_2$, except that before addition of the glufosinate 10 mL of 30% H_2O_2 was added to oxidize the complex to Co(III). Following the second reflux and the addition of CH_3CN , a violet solid material was precipitated; however, it was intensely hygroscopic, and an elemental analysis was not performed. The complex could be eluted as a single band from an anion-exchange column with 0.3 M NaCl as eluent, as would be expected for a uninegative complex.

Iron(II) and iron(III) were also coordinated by glufosinate, yielding the same complex in both cases, probably iron(III). A solid was precipitated by addition of CH_3CN but was strongly contaminated with salt. The material was soluble in water.

Instrumental Measurements. EDXRF spectra were recorded with a Hitachi 5100M X-ray energy spectrometer. The EDXRF spectra allowed a qualitative analysis for nontrace amounts of elements above Na in atomic number. Powder X-ray diffraction spectra were recorded with a Phillips APD-3600 automated diffractometer. Infrared spectra were measured on a Mattson Cygnus 25 FTIR spectrometer using KBr pellets. UV-visible absorption spectra were recorded with a Hewlett-Packard Model 8451 diode array spectrometer.

RESULTS AND DISCUSSION

A central question for all the glufosinate complexes prepared concerns the groups coordinated to the metal ion. Infrared spectroscopy provides the most useful spectroscopic tool. The diagnostic bands between 400 and 4000 cm^{-1} are listed in Table I together with their assignments.

Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105.

Table I. Selected Infrared Frequencies (cm⁻¹) for Metal Complexes of Glufosinate

complex	$\nu_{as}(\text{CO}_2)$	$\delta(\text{NH}_2)$	$\nu_s(\text{PO}_2)$	$\nu_{as}(\text{PO}_2)$
$\text{K}_{0.5}(\text{NH}_4)_{0.5}[\text{Cr}(\text{gluf})_2] \cdot 3\text{H}_2\text{O}$	1632	<i>a</i>	1036	1145
$[\text{Ni}(\text{gluf})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	1640	<i>a</i>	1040	1110
$[\text{Cu}(\text{gluf})]$	1637	1606	1050	1136
$[\text{Mg}(\text{gluf})] \cdot 4\text{H}_2\text{O} \cdot 5\text{CH}_3\text{OH}$	1605	<i>a</i>	1026	1112
$\text{K}[\text{Co}(\text{gluf})_2]$	1632	<i>a</i>	1032	1123
NH_4Hgluf	1725	1540	1035	1125

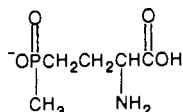
^a Obscured by intense carboxylate stretching band.

Table II. Electronic Spectral Data of Metal Complexes with Glufosinate in Aqueous Solution

complex	$\lambda_1 (\epsilon_{\text{max}})^a$	$\lambda_2 (\epsilon_{\text{max}})^a$
$[\text{Cr}(\text{gluf})_2]^-$	562 (45)	408 (39)
$[\text{Co}(\text{gluf})_2]^-$	524	
$[\text{Ni}(\text{gluf})(\text{H}_2\text{O})_2]$	618 (2.4)	362 (4.0)
$[\text{Cu}(\text{gluf})]$	722 (34)	

^a Units: λ , nm; ϵ , M⁻¹ cm⁻¹.

The Hgluf⁻ used (as the NH₄⁺ salt) in the syntheses has the structure



During complex formation 2 equiv of base was added, deprotonating the ammonium ion and the carboxylic acid.

In all of the metal complexes except that of Mg²⁺, the asymmetric carboxylate stretching frequency is found between 1630 and 1640 cm⁻¹. This is characteristic of coordinated carboxylate ligands (Nakamoto, 1978). The asymmetric stretching frequency in the molecular carboxylic acid is generally found about 100 cm⁻¹ higher in energy, and for glufosinate (NH₄Hgluf) this band is located at 1725 cm⁻¹. An uncomplexed, deprotonated carboxylate, as might be found in a sodium salt, for example, generally has this band shifted to about 1560 cm⁻¹ (Nakamoto, 1978). The presence of $\nu_{as}(\text{CO}_2^-)$ at 1605 cm⁻¹ in [Mg(gluf)] can be taken as an indication that coordination to the magnesium ion is not as strong as to the transition-metal ions. This is consistent with the substantial dissociation of the complex in aqueous solution.

Amine coordination can be established by the shift of an NH₂ bending mode, normally found near 1500 cm⁻¹ in uncomplexed amines, to higher frequencies in metal complexes (Nakamoto, 1978). For NH₄Hgluf this band is found at 1540 cm⁻¹. Only in the copper(II) complex can the shifted band be seen (at 1606 cm⁻¹), because the carboxylate stretching band is broad and obscures the less intense $\delta(\text{NH}_2)$ band. However, the 1540-cm⁻¹ band is clearly missing in all the complexes studied, and it is appropriate to conclude that the amine is coordinated in all cases.

The two strong bands at about 1050 and 1150 cm⁻¹ are considered to be characteristic bands of the phosphinate group, representing a P-O stretching mode. These bands may be shifted up to 35 cm⁻¹ in either direction upon coordination to metal ions (Tsuboi, 1957). From Table I it can be seen that substantial shifts take place for all the complexes except that of cobalt(III). We suspect that the phosphinate moiety is nevertheless coordinated to Co(III). However, since the complex was intensely hygroscopic, it is possible that water displaces the phosphinate on contact.

The electronic spectral data of the transition-metal glufosinate complexes in aqueous solution are tabulated in Table II. Some structural conclusions can be reached

from these data. The nickel complex, although coordinated by only one glufosinate ligand, appears to have a total coordination sphere that is close to octahedral. Extinction coefficients as low as those observed for this complex are very rare for tetrahedral or other geometries (Lever, 1984). However, since analysis shows there to be only 1.5 water molecules per nickel, even if the glufosinate were tetradentate there would not be enough H₂O to fill in the coordination sphere if the complex were a monomer. We therefore suggest that it is at least a dimer, and possibly a higher oligomer. If it is a dimer, then the most likely structure is one in which the glufosinate occupies four coordination sites and the other two sites are filled by bridging water molecules. If a linear-chain oligomer is formed, the bridging may be accomplished by the glufosinate ligand itself, provided two sites on one atom are occupied by a phosphinate and two sites on the connected atom by the carboxylate group. Five sites would thus be taken up by glufosinate, and a nonbridging water molecule could occupy the sixth. At this time we favor the dimer structure because the ready solubility in water seems less consistent with oligomer formation.

The copper(II) compound crystallizes with no additional water molecules. The spectrum in solution is typical of Cu(II) complexes, which are characterized by square-planar coordination, usually with something occupying more distant axial positions: water molecules when in solution or a ligand atom from an adjacent complex in the solid state. All four of the square-planar positions in [Cu(gluf)] must be occupied by atoms from the glufosinate, presumably a carboxylate oxygen, the amine nitrogen, and the two oxygens from the phosphinate group. Molecular models indicate that it is possible for tetradentate square-planar coordination by glufosinate to occur. Another possibility, however, is that a chain structure is involved. Once again, we favor the assignment to a monomeric unit, because this is more consistent with the solubility of the complex in water.

The moderate conductivity of [Cu(gluf)] in water could arise from an equilibrium involving the dissociation of the complex to form Cu²⁺ and gluf²⁻, which is consistent with the normally high lability of copper(II). It may also be the result of an acid-base equilibrium in which one of the glufosinate groups is displaced by water and the dangling group protonated to form a unipositive complex.

Both Co(III) and Cr(III) have strong tendencies toward six-coordination, and the electronic spectra of the glufosinate complexes are consistent with this. In both cases glufosinate acts as a tridentate ligand. The three coordinating groups most probably adopt a facial rather than a meridional arrangement, since the latter is usually characterized by a much larger extinction coefficient for the first spin-allowed band in the electronic spectrum (Subramaniam et al., 1988). Several geometric isomers are possible, but the data are insufficient to make assignments.

CONCLUSIONS

Glufosinate, like glyphosate, coordinates strongly with a number of metal ions. There are also parallels in the adoption of a tridentate or tetradentate mode of coordination. Both glufosinate and glyphosate (Subramaniam and Hoggard, 1988), for example, coordinate to nickel(II) as tetradentate ligands. One very large difference exists, however: neutral complexes containing glyphosate are quite insoluble in water, while the analogous complexes of glufosinate are more easily dissolved.

The implications for groundwater contamination are not entirely clear. Glyphosate is complexed and precipitated by the metal ions found in heaviest concentration in

groundwater: Ca^{2+} , Mg^{2+} , Fe^{2+} , and Fe^{3+} , among others. The same ions are coordinated by glufosinate. Some of these complexes are thermodynamically quite stable, as evidenced by the negligible conductivities in aqueous solution. Nevertheless, at low concentration none of the glufosinate complexes examined precipitate, but remain in solution. It is uncertain whether any complexation occurs at the still lower concentrations that would be likely in groundwater, since equilibrium constants for glufosinate complex formation have not been measured.

If some complexation does occur, whether this yields an increased risk or is in fact beneficial, depends on many factors involving a comparison of properties of the metal complexes with those of free glufosinate: transport properties through, and interactions with, soils, mammalian toxicities, and degradation mechanisms, to name a few. However, to the extent that the metal complexes remain intact in dilute solution, deactivation of both herbicidal and zootoxic activity seems likely, provided that some of the more stable complexes are also kinetically inert. On the other hand, kinetically labile metal complexes may provide a transport mechanism within the plant that enhances herbicidal activity.

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Registry No. Mg, 7439-95-4; Cu, 7440-50-8; Ni, 7440-02-0; Fe^{2+} , 15438-31-0; Fe^{3+} , 20074-52-6; $[\text{Mg}(\text{gluf})]$, 121098-49-5; $[\text{Cu}(\text{gluf})]$, 121098-50-8; $[\text{Ni}(\text{gluf})(\text{H}_2\text{O})]$, 121098-51-9; $\text{K}_{0.6}(\text{NH}_4)_{0.5}[\text{Cr}(\text{gluf})_2]$, 121124-92-3; $[\text{Co}(\text{gluf})_2]$, 121124-93-4; Cr, 7440-47-3; Co, 7440-48-4.

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Uptake and Metabolic Fate of Indole in Soybeans Grown in Hydroponic Solutions and Soil¹

Robert J. Fellows,* Roger M. Bean, and Dominic A. Cataldo

Indole, a neutral aromatic heterocycle, was studied to determine its rate and patterns of uptake as well as its metabolic fate in soybeans grown in solution culture and soil. Indole was rapidly accumulated from amended nutrient solutions with an apparent $K_s = 0.304$ mM and $V_{\text{max}} = 86.9$ μg of indole/h per g fresh weight root. Free indole, however, was no longer detected inside the plant within 48 h following exposure. Radiochromatography and additional analysis indicated that the material was not volatilized from the foliage but instead was rapidly converted to tryptophan and subsequently metabolized. Soil studies indicated that >80% of the amended indole was bound in a nonextractable form within 24 h. Uptake of label by soybeans from ^{14}C indole-amended Hagerstown soil, a high clay-low organic matter soil, was 3-7 times greater than from Palouse soil, a low clay-high organic matter soil. Analysis of the plant tissues indicated label distribution patterns of the Hagerstown plants were similar to those of the ^{14}C indole-amended plants grown in solution culture, while the Palouse plants resembled those grown in ^{14}C tryptophan-amended solution culture. The higher organic matter content of the Palouse soil may have contributed to increased metabolic transformation of the bioavailable form of the indole, thus altering the uptake rates.

Growing concern has emerged over the uncontrolled release of organic chemicals and their potential health and

environmental effects as they migrate through soils to surface or ground waters. Terrestrial plants are capable of intercepting these materials via direct root uptake (Chaney, 1983) and are an important link between these soil mobile waste forms and the food web leading to man. It is, therefore, important to consider those processes that affect the potential of terrestrial plants to accumulate, modify, or recycle organic xenobiotics back into the en-

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