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Metal Complexes of Picloram

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Insoluble complexes of picloram with nickel(II) and iron(II) are formed at near-neutral pH. This presents a mechanism for the possible removal of picloram from contaminated ground water, naturally or intentionally.

Picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid = Hpcl) is a widely used herbicide for control of perennial weeds and shrubs. It has been the herbicide of choice in some statewide leafy spurge control programs. Although its mammalian toxicity is relatively low, it is not easily degraded microbially (Foy, 1976), and therefore its persistence in the soil is of some concern. In surface waters photochemical degradation pathways do exist (Hedlund and Youngson, 1972; Skurlatov, 1983). Its solubility in water is moderate, 430 ppm (Weed Science Society of America, 1970). It is, however, usually applied as the much more water-soluble potassium salt, and in any case the free acid is converted to the anion in near-neutral or alkaline soils with even modest buffering capacity. Picloram should thus be highly mobile, and experimental studies have confirmed this (Baur et al., 1972). The obvious problems that can result if substantial amounts reach the ground water have spurred studies in geographic areas subject to intensive spraying (Glatt, 1985; Lym and Messersmith, 1986).

The pyridine-2-carboxylic acid functionality is well-known to coordinate metal ions strongly (Anderegg, 1960; Yuen et al., 1983). The consequences of metal ion coordination by picloram, aside from the biochemical implications for herbicidal activity, are not obvious a priori. Mobility may be increased or decreased. Depending on the lability of the complex formed, toxicity might be increased, decreased, or unaffected.

An earlier study showed relatively weak complex formation in solution between picloram and Fe(III) or Cu(II) (Chang and Foy, 1982). We report here the much stronger interaction with Fe(II) and Ni(II) ions under pH conditions closer to those in soils, and we discuss the implications for ground water contamination.

EXPERIMENTAL SECTION

Technical-grade picloram (free acid) was provided by Dow Chemical Co. It was recrystallized prior to use by

Table I. Infrared Data on Metal-Picloram Complexes

	$\nu_a(\text{COO})$	$\nu(\text{py})^a$	$\nu(\text{py})^b$
HPcl	1705 vs	642 m	431 m
Ni(pcl) ₂	1626 vs	658 w	484 w
Fe(pcl) ₂	1611 vs, 1640 w, 1674 w	654 w	459 w

^a In-plane ring deformation. ^b Out-of-plane ring deformation.

slowly dissolving in warm (50 °C) methanol to saturation. Decolorizing charcoal was added and heating continued for 15 min. After filtration the solution was cooled and half the solvent was allowed to evaporate. The cream-colored crystalline picloram was filtered off and dried in a vacuum desiccator.

Ni(pcl)₂·4.5H₂O. Ni(NO₃)₂·6H₂O (2.9 g, 0.010 mol) was dissolved in 25 mL of H₂O. Picloram (4.8 g, 0.020 mol) and 0.80 g (0.020 mol) of NaOH were dissolved in warm absolute ethanol. The two solutions were combined. Upon cooling, a lime green crystalline precipitate was collected. It was soluble in EtOH and in water. Upon recrystallization twice from water and air-drying, the yield was 0.5 g. After air-drying for several days, the compound was no longer soluble in water or alcohols. Anal. Calcd for Ni(C₆H₂Cl₃N₂O₂)₂·4.5H₂O: C, 23.20; H, 2.09; N, 9.02; Cl, 34.31; Ni, 9.46. Found: C, 23.79; H, 2.21; N, 8.94; Cl, 34.48; Ni, 9.24.

Fe(pcl)₂·H₂O. FeSO₄·7H₂O (3.1 g, 0.010 mol) was dissolved in 25 mL of H₂O. Picloram (4.8 g, 0.020 mol) and 0.80 g (0.020 mol) of NaOH were dissolved in 25 mL of warm EtOH. When the two solutions were mixed, a burnt orange precipitate formed. This was insoluble in water, alcohols, CH₃CO₂H, CH₃CN, and DMSO. After the precipitate was washed with MeOH and air-dried, the yield was 4.5 g. Anal. Calcd for Fe(C₆H₂Cl₃N₂O₂)₂·H₂O: C, 25.95; N, 10.09; Cl, 38.39; H, 1.08; Fe, 10.07. Found: C, 26.05; N, 10.05; Cl, 38.49; H, 1.25; Fe, 10.03.

Instrumentation. X-ray powder diffraction spectra (Philips APD-3600) were recorded to confirm the crystallinity of the two complexes. Infrared spectra were measured on a Mattson Cygnus FTIR spectrometer and UV-visible spectra on a Hewlett-Packard 8451 diode array spectrometer.

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RESULTS AND DISCUSSION

The high melting points (>280 °C) of the $M(\text{pcl})_2$ compounds indicate a basically ionic crystal structure. Picloram is not simply a counterion, however. Infrared data (Table I) show that both the pyridine nitrogen and carboxylate oxygen are coordinated. A general criterion for carboxylate coordination is the presence of a strong carbonyl stretching frequency between 1610 and 1670 cm^{-1} (Nakamoto, 1978). A band above 1700 cm^{-1} is typical of a protonated, uncoordinated COOH group, while an unprotonated COO^- is generally found between 1560 and 1580 cm^{-1} . No uncoordinated carboxylate could be detected in the IR spectrum.

A diagnostic test for pyridine coordination is a shift of ring-stretching modes at 604 and 405 cm^{-1} in pyridine to higher frequencies (Clark and Williams, 1965; Nakamoto, 1978). These bands are at 625 and 419 cm^{-1} in pyridine-2-carboxylic acid (picolinic acid, Hpic) and at 642 and 431 cm^{-1} in picloram. The carboxylate, amino, and chloro groups cause a shift to higher frequencies but add no obscuring peaks. Coordination to Fe(II) and Ni(II) shifts these bands to still higher frequencies, as expected.

The nickel complex might, from its stoichiometry, appear to share characteristics with the picolinate complex, $\text{Ni}(\text{pic})_2 \cdot 4\text{H}_2\text{O}$. However, the latter is blue, is soluble in water, and contains two water molecules in an approximately octahedral coordination sphere (Loiseleur et al., 1967). The green of $\text{Ni}(\text{pcl})_2$ points toward a different coordination environment, quite possibly one in which the fifth and sixth sites are taken by amino or chloro groups from neighboring rings or, as may be presumed for the green dehydrated $\text{Ni}(\text{pic})_2$ (Wheeler et al., 1978), by the carbonyl oxygens from adjacent rings. This network solid-state structure would account for its low solubility.

Although neither complex is soluble to any detectable extent in water, picloram can still be replaced by a stronger ligand, such as dimethylglyoxime (dmg). The characteristic red precipitate of $\text{Ni}(\text{dmg})_2$ forms over a period of about 20 s. Likewise, edta^{4-} causes the dissolution of $\text{Ni}(\text{pcl})_2$ and formation of the blue $[\text{Ni}(\text{edta})]^{2-}$ complex over a 20-s period. $\text{Fe}(\text{pcl})_2 \cdot \text{H}_2\text{O}$ will also dissolve in the presence of edta^{4-} , although the reaction is about 50 times slower.

The solubility products of both $\text{Ni}(\text{pcl})_2$ and $\text{Fe}(\text{pcl})_2$ are evidently quite small. Spectrophotometrically, 10^{-7} M concentrations of free or complexed picloram can be detected, but no traces were found in water that had been agitated with either complex. Thus, $K_{\text{sp}} < 10^{-21}$. This suggests that picloram (which will be in the anion form at a pH corresponding to soil or ground water conditions) may well eventually be precipitated by nickel(II) and especially iron(II), depending, of course, on just how small the solubility products are. It should be noted that the pH of the reaction mixtures used to prepare these complexes was generally near 6.

Experiments with iron(III) also yielded insoluble complexes, from which we have not obtained uniform analyses. Iron levels in ground water tend to be rather high. Chemical analysis of ground water from several North Dakota sites yielded an average iron content of about 3 ppm (Harkness and Haffield, 1982), or 5×10^{-8} M. No distinction was made in these analyses between ferrous and ferric states. The situation will also be complicated by

complexation with other metal ions.

Further studies are required to quantify the various equilibria, but our conclusion at this point is that metal ion complexation, particularly with iron(II), serves as a mechanism to remove picloram from solution once it reaches the ground water, if not before. Treatment of actual spill sites might also be undertaken by purposeful addition of benign metal salts.

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