Binding Ability of Pesticides. X-ray, Spectroscopic, and Polarographic Studies of the Cu(II) Interaction with Acifluorfen[†]

Henryk Kozłowski,[‡] Alba Pusino,[*,§] Jolanta Swiatek,[∥] Jan Spychała,[∥] Tadeusz Glowiak,[‡] Giovanni Micera,[⊥] and Carlo Gessa[§]

Institute of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland, Istituto di Chimica Agraria, Università di Sassari, Via E. De Nicola 10, 07100 Sassari, Italy, Department of Basic Medical Sciences, Medical Academy of Wrocław, J. Kochanowskiego 14, 51603 Wrocław, Poland, and Dipartimento di Chimica, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy

The copper(II) complexes formed by the herbicide Acifluorfen [5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid] in aqueous solution have been studied by polarographic techniques. The herbicide binds the metal ion acting mainly as a carboxylic ligand, although the simultaneous involvement of the nitro group is suggested by the value of the measured stability constant. Rather insoluble complexes having a dimetallic structure of the tetra-μ-acetatodiaquadicopper(II) type, as determined by single-crystal X-ray diffraction, precipitate from more concentrated solutions.

INTRODUCTION

Our previous studies on the interaction of metal ions with pesticides have shown that these compounds widely used in agriculture can form stable complex species with metal ions (Decock et al., 1985; Lerivrey et al., 1986; Pusino et al., 1988). Metal ions, on the other hand, may affect remarkably the fate of pesticides, e.g., catalyze their decomposition (Pusino et al., 1988) or inactivate them (Hensley et al., 1978). Among others, the Cu(II) ion is very active in influencing pesticide chemistry and biochemistry, due to its efficient binding ability. The herbicide Acifluorfen [5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid (AF)] is provided with a carboxylate
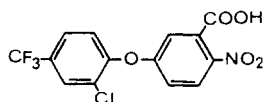
group which, although not very effective in principle, is a potential binding site for metal ions. Besides, the presence of a neighboring nitro group could stabilize the complex formed between the Cu(II) ion and the pesticide molecule.

The results obtained in our laboratory indicate that this herbicide can precipitate the saturating metal ions of soil clays by forming complexes sparingly soluble in water. This molecule acts as a complexing agent also in the soil solution, although the involved species are still unknown.

The purpose of this work was to describe the copper(II)–AF chemistry to obtain the basic information needed to fully understand the Acifluorfen interaction with metal ion bearing soil components. Therefore, the complex species formed in dilute aqueous solution were investigated by using polarography. The solid compound precipitated from more concentrated solutions was examined by single-crystal X-ray diffraction and spectroscopic techniques.

MATERIALS AND METHODS

Materials. Acifluorfen was obtained by acidification of an aqueous solution of sodium Acifluorfen (Rhone-Poulenc AG Co.) with 1 N HCl. The acid was filtered off and recrystallized from benzene–petroleum ether, mp 157–162 °C (Johnson et al., 1978).

Polarography. Polarographic experiments were performed by using a PP-04 instrument (Telpod) in direct current (DC, TAST) and differential pulse polarography (DPP) modes. All experiments employed a three-electrode system with a dropping mercury electrode (DME), as a working electrode, a platinum wire as an auxiliary electrode, and a saturated calomel reference electrode. The drop time was 3 s. The DPP measurements on a hanging mercury drop electrode (HMDE) were carried out on a PA-4 polarographic analyzer by using a three-electrode configuration with platinum counter and saturated calomel reference electrodes. A pulse amplitude of 50 mV was applied in DPP measurements. Aqueous solutions containing 5×10^{-5} M Cu^{2+} were titrated with 20–140 μL of 5×10^{-3} or 10^{-2} M alcoholic solutions of Acifluorfen. The metal-to-ligand molar ratios ranged from 4:1 to 1:24. The measurements were carried out at 20 °C over the pH range 4.9–5.2 (I = KNO_3, 0.20 M, or $NaClO_4$, 0.15 M). The solutions were purged with argon for 10 min before measurements to remove dissolved oxygen.

Preparation of the Complexes. The copper complex was obtained by preparing an equimolar (1×10^{-3} mol in 5 mL, pH 5.77) aqueous solution of sodium Acifluorfen and $CuCl_2$. A precipitate was obtained at room temperature almost immediately after the reactants were mixed. After filtering, washing with EtOH, and air drying, the powderlike compound was analyzed as $[Cu(C_{14}H_6ClF_3NO_5)_2(H_2O)]_2 \cdot 2H_2O$. Anal. Calcd for $C_{28}H_{16}Cl_2CuF_6N_2O_{12}$: C, 40.97; H, 1.96; N, 3.41; H_2O, 4.4. Found: C, 41.22; H, 1.94; N, 3.38; H_2O, 4.0. By recrystallization from EtOH suitable crystals having the formula $[Cu(C_{14}H_6ClF_3NO_5)_2(C_2H_5OH)]_2$ separated. Anal. Calcd for $C_{30}H_{18}Cl_2CuF_6N_2O_{11}$: C, 43.36; H, 2.18; N, 3.37, C_2H_5OH, 5.54. Found: C, 43.40; H, 2.15; N, 3.41; C_2H_5OH, 5.5.

Crystallographic Measurements. Approximate unit-cell dimensions were determined from rotation and Weissemberg photographs. A specimen of $0.45 \times 0.55 \times 0.70$ mm was selected for diffraction studies. More accurate cell dimensions and an orientation matrix used for data collection were obtained by a least-squares analysis of the diffractometer settings of 15 high-order Mo $K\alpha$ reflections measured on a Syntex P2$_1$ computer-controlled four-circle diffractometer equipped with a scintillation counter and a graphite monochromator. The intensities of 5590 independent reflections were measured at room

[‡] University of Wrocław.
[§] Istituto di Chimica Agraria, Università di Sassari.
[∥] Medical Academy of Wrocław.
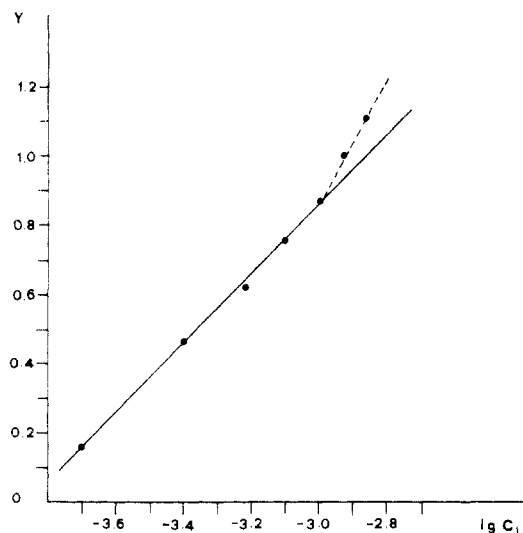[⊥] Dipartimento di Chimica, Università di Sassari.

1990 *J. Agric. Food Chem.*, Vol. 38, No. 10, 1990

Kozłowski et al.

Figure 1. De Ford–Hume approximation according to the equation $y = \log \beta_N + N \log C_L$, where $y = (0.4343nF\Delta E_p)/RT)$ + $\log (i_p/i_{pk})$, i_{pk} and i_p are the limiting currents of Cu(II) reduction wave before and after the addition of ligand, respectively; ΔE_p is the difference of half-wave potential; and C_L is the ligand concentration.

temperature by the ϑ–2ϑ scan technique, up to a $2\vartheta_{max}$ value of 48°. Two standards were monitored after every 50 reflections. The maximum variation of the intensity value was 6%. The intensities were corrected for Lorentz and polarization effects, not for absorption; 3355 reflections with $I > 3.56\sigma(I)$ were used for structure determination. The structure was solved by direct methods using the SHELX-76 set of programs (Sheldrick, 1976) and refined by the full-matrix least-squares technique. All the hydrogen atoms were placed at computed positions, as determined from the successive Fourier difference maps. The refinement of coordinates and thermal parameters (anisotropic for non-hydrogen and isotropic for hydrogen atoms) converged at $R = 0.059$, $R_w = 0.063$, and $w = 1/\sigma^2(F)$. Neutral atomic scattering factors for all atoms were taken from the *International Tables for X-ray Crystallography* (1974), and the calculations were performed on a PC/AT computer using the Syntex (1976) XTL/XTLE structure determination package. Crystallographic data: $C_{60}H_{36}Cl_4Cu_2F_{12}N_4O_{22}$; monoclinic, $I2/a$; $a = 28.000(7)$, $b = 14.855(3)$, $c = 17.320(4)$ Å and $\beta = 100.20(3)°$; $V = 7090.2(3)$ Å^3; $M = 1659.83$, $Z = 4$; $D_m = 1.55$ and $D_c = 1.555$ g cm^{-3}.

Physical Measurements. X-band ESR spectra were recorded on a Varian E9 instrument at 110 K. Infrared spectra (KBr disks) were obtained with a Perkin-Elmer 683 spectrophotometer. Microanalyses (C, H, and N) were performed on a Perkin-Elmer 240 B analyzer. The water and EtOH content in the solid complexes was determined by thermogravimetry using a Perkin-Elmer TGS-2 apparatus under a nitrogen atmosphere at a scanning rate of 2 °C min^{-1}.

RESULTS AND DISCUSSION

Polarographic Analysis. The data obtained by three different techniques, DPP on either a dropping mercury electrode or a hanging mercury drop electrode and DC TAST, indicate that the preponderant complex formed between Cu(II) and AF in dilute solution is the equimolar Cu(AF) species. The stability constant for this complex was calculated by direct calculations using the concentration of unbound and bound metal ion or by the De Ford–Hume (De Ford and Hume, 1951) method (Figure 1 and Table I). Almost the same value was given by the two different methods (Table II), confirming the reliability of the experimental approach used.

The only major binding site available to copper in the formed complex is the carboxylate group, as supported also by the crystal structure determination of the solid complex

Table I. Peak Potentials (E_p) and Peak Currents (i_p) for the Copper(II) Complexes with Acifluorfen as a Function of the Ligand Concentration (C_L)[a]

C_L, M	E_p, V	i_p, mm
0	0.018	108.0
1.9960×10^{-4}	0.016	87.0
3.9841×10^{-4}	0.010	67.5
5.9642×10^{-4}	0.008	56.0
7.9365×10^{-4}	0.006	48.0
9.9010×10^{-4}	0.004	42.0
1.1858×10^{-3}	0.002	36.5
1.3807×10^{-3}	0.000	33.0

[a] $C_{Cu^{2+}} = 5 \times 10^{-5}$ M; $I = 0.15$ M NaClO$_4$.

Table II. Stability Constants (log β) Evaluated from Polarographic Measurements for Cu(II)-AF Species

technique	species	log β
DPP-HMDE	Cu(AF)	3.23[a]
DC-TAST	Cu(AF)	3.18[a]
DPP-DME	Cu(AF)	3.20[a]
DPP-DME	Cu(AF)	3.18[b]
DPP-DME	Cu(AF)$_2$	5.80[c]

[a] Stability constant calculated from measurements of the free metal concentration directly from the decrease of the limiting current of the metal reduction wave. [b] Stability constant calculated according to the De Ford–Hume approach (Figure 1). [c] See text for comments.

(vide infra). The stability value, log β = 3.2, calculated for the solution species is, however, significantly higher, by more than 1 order of magnitude, than those usually observed for equimolar copper complexes with pure carboxylate coordination, e.g., log β = 1.5–1.8 [see Micera et al. (1989) and references cited therein]. This increase in stability may indicate that in the Cu(AF) species also the nitro group takes part in metal binding. This mode of coordination would lead to the formation of a chelate ring, with a consequent increase in the stability of the formed species. The plot shown in Figure 1 also indicates that, in the presence of a high excess of ligand, other complex species may be formed (see the two experimental points obtained at the highest ligand concentration). The estimation based on these points indicates the formation of the Cu(AF)$_2$ species with log β = 5.8. These evaluations are, however, very rough because they are based on too few experimental points. In addition, the high ligand excess causes the polarograms to be badly resolved, due to an increase of viscosity in solution and the reduction waves of the metal ion to exhibit local maxima, thus hindering a precise evaluation of the experimental data.

Crystallographic Results. The final positional parameters for the computed structure are listed in Table III. A view of the complex is presented in Figure 2, whereas relevant bond lengths are listed in Table IV. The crystal structure of the compound is composed of centrosymmetric dimers. Four bidentate carboxylate anions form bridges between isolated pairs of copper atoms separated by 2.660(1) Å. The structure is closely related to that of the most representative complex of this type, tetra-μ-acetatodiaquadicopper(II) (Brown and Chidanbaram, 1973; De Meester et al., 1973), where the Cu–Cu separation is 2.62 Å. The coordination about the Cu atom is square pyramidal, neglecting the Cu–Cu interaction. The fifth position is occupied by a weakly bound ethanol molecule with a Cu–O distance of 2.122(7) Å [the Cu–O(H$_2$O) apical distance in the acetate complex is 2.16 Å]. The copper atoms are displaced toward the ethanol molecule from the plane containing the four carboxylate oxygens, as indicated by the O(carbox)–C–O(EtOH) angles. The mean Cu–O (carboxylate) bond length is 1.96 Å, which is almost the same value (1.97 Å) as that found for the corresponding

Binding Ability of Pesticides

J. Agric. Food Chem., Vol. 38, No. 10, 1990 **1991**

Table III. Unit-Cell Positional and Thermal (Å²) Parameters and Their ESD's[a]

	x	y	z	B_{eq}
Cu	0.2679 (1)	0.2173 (1)	0.6896 (1)	3.1 (1)
Cl(1)	0.0736 (1)	0.6059 (2)	0.5084 (2)	6.8 (1)
Cl(2)	0.1096 (1)	−0.1464 (2)	0.5361 (2)	8.4 (2)
O(1)	0.2553 (2)	0.3392 (3)	0.6481 (3)	3.8 (2)
O(2)	0.2252 (2)	0.3953 (3)	0.7511 (3)	4.1 (3)
O(3)	0.1643 (2)	0.5735 (4)	0.5405 (3)	4.8 (3)
O(4)	0.3047 (2)	0.5160 (4)	0.7695 (4)	6.3 (3)
O(5)	0.2727 (2)	0.6415 (4)	0.7934 (4)	8.2 (4)
O(6)	0.2000 (2)	0.1859 (3)	0.6453 (3)	4.0 (2)
O(7)	0.1698 (2)	0.2405 (3)	0.7479 (3)	3.9 (2)
O(8)	0.0433 (2)	−0.0287 (4)	0.6011 (4)	7.4 (4)
O(9)	0.1295 (2)	0.3615 (4)	0.6185 (4)	7.8 (4)
O(10)	0.0532 (3)	0.3877 (5)	0.6159 (6)	11.1 (5)
O(11)	0.2992 (3)	0.1656 (6)	0.5957 (4)	8.8 (4)
F(1)	0.0025 (3)	0.2784 (6)	0.3893 (4)	14.0 (5)
F(2)	0.0264 (3)	0.2741 (6)	0.2855 (5)	15.5 (6)
F(3)	−0.0222 (3)	0.3677 (6)	0.3088 (6)	16.8 (6)
F(4)	0.0976 (3)	−0.3366 (6)	0.8450 (5)	14.9 (6)
F(5)	0.1440 (4)	−0.3640 (5)	0.7742 (5)	16.1 (6)
F(6)	0.1632 (3)	−0.2706 (5)	0.8635 (5)	14.4 (5)
N(1)	0.2760 (2)	0.5767 (4)	0.7509 (4)	4.9 (3)
N(2)	0.0880 (3)	0.3363 (5)	0.6176 (5)	6.6 (4)
C(1)	0.2378 (3)	0.4005 (5)	0.6837 (5)	3.8 (4)
C(2)	0.2289 (3)	0.4902 (5)	0.6407 (5)	3.4 (3)
C(3)	0.2447 (3)	0.5728 (5)	0.6732 (5)	3.8 (4)
C(4)	0.2336 (3)	0.6527 (5)	0.6337 (5)	4.6 (4)
C(5)	0.2069 (3)	0.6514 (5)	0.5590 (5)	4.6 (4)
C(6)	0.1909 (3)	0.5700 (5)	0.5271 (5)	3.7 (4)
C(7)	0.2020 (3)	0.4896 (5)	0.5659 (5)	3.8 (4)
C(8)	0.1298 (3)	0.5078 (5)	0.4282 (5)	4.0 (4)
C(9)	0.0847 (3)	0.5180 (5)	0.4488 (5)	4.3 (4)
C(10)	0.0476 (3)	0.4600 (6)	0.4193 (5)	4.6 (4)
C(11)	0.0573 (3)	0.3897 (6)	0.3714 (5)	4.8 (4)
C(12)	0.1029 (3)	0.3789 (6)	0.3518 (5)	5.2 (5)
C(13)	0.1389 (3)	0.4395 (6)	0.3807 (5)	5.0 (4)
C(14)	0.0183 (4)	0.3261 (7)	0.3380 (6)	7.7 (6)
C(15)	0.1663 (3)	0.2051 (5)	0.6816 (4)	3.6 (4)
C(16)	0.1147 (3)	0.1792 (5)	0.6431 (4)	3.5 (3)
C(17)	0.0779 (3)	0.2392 (5)	0.6159 (5)	4.0 (4)
C(18)	0.0315 (3)	0.2123 (6)	0.5850 (5)	5.3 (4)
C(19)	0.0209 (3)	0.1220 (6)	0.5803 (5)	5.3 (5)
C(20)	0.0565 (3)	0.0606 (5)	0.6070 (5)	4.7 (4)
C(21)	0.1035 (3)	0.0855 (5)	0.6391 (5)	4.4 (4)
C(22)	0.0665 (3)	−0.0910 (5)	0.6559 (6)	5.7 (5)
C(23)	0.0978 (3)	−0.1539 (6)	0.6298 (5)	5.3 (5)
C(24)	0.1177 (3)	−0.2208 (6)	0.6798 (5)	5.4 (4)
C(25)	0.1072 (3)	−0.2251 (6)	0.7530 (5)	5.7 (5)
C(26)	0.0776 (4)	−0.1643 (7)	0.7796 (6)	7.5 (6)
C(27)	0.0569 (4)	−0.0967 (7)	0.7308 (6)	7.7 (6)
C(28)	0.1261 (4)	−0.2978 (7)	0.8086 (7)	8.8 (7)
C(29)	0.3529 (12)	0.1480 (19)	0.5698 (11)	32.7 (27)
C(30)	0.3632 (7)	0.0948 (13)	0.6332 (11)	17.9 (14)
H(1)	0.245	0.712	0.660	6.0
H(2)	0.200	0.711	0.527	6.0
H(3)	0.191	0.431	0.540	6.0
H(4)	0.014	0.467	0.435	6.0
H(5)	0.110	0.327	0.317	6.0
H(6)	0.172	0.435	0.364	6.0
H(7)	0.005	0.260	0.566	6.0
H(8)	−0.014	0.101	0.558	6.0
H(9)	0.129	0.043	0.661	6.0
H(10)	0.141	−0.267	0.663	6.0
H(11)	0.072	−0.170	0.839	6.0
H(12)	0.034	−0.055	0.753	6.0

[a] $B_{eq} = {}^1/_3 \sum_i \sum_j B_{ij} a_i{}^* a_j{}^* a_i a_j$.

acetate complex. The bond parameters of the carboxylate groups are normal (C–O bond length of 1.25–1.28 Å) and similar to those of the bridging acetate ligand.

Magnetic and Spectroscopic Results. The ESR spectra of both the crystalline and powderlike compounds ($g_{\parallel} = 2.36$, $g_{\perp} = 2.08$, $D = 0.34$ cm^{-1}, see Figure 3) are typical of Cu(II) dinuclear carboxylate complexes without a strong interdimeric exchange interaction, e.g., isolated Cu–Cu couples, accordingly with the observed crystal
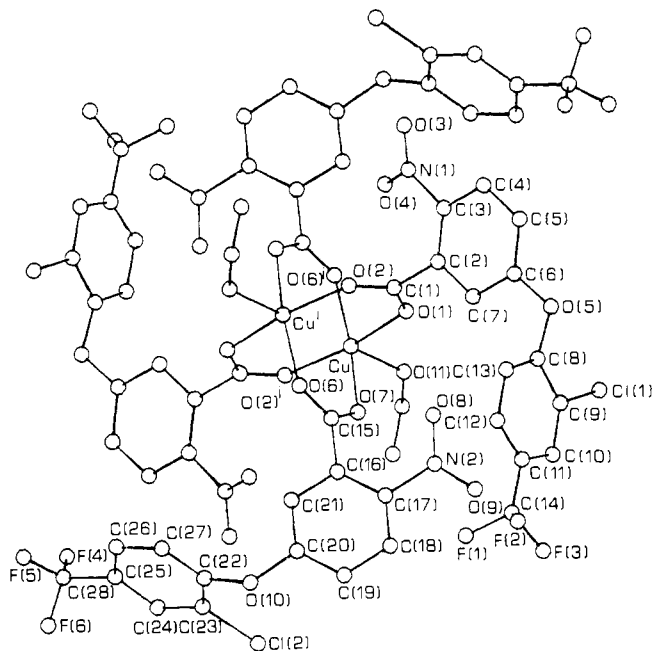
Figure 2. Atomic numbering and molecular structure of the complex Cu$_2$(AF)$_4$(EtOH)$_2$.

Table IV. Selected Bond Distances (Angstroms) and Angles (Degrees) with Their ESD's[a]

Distances			
Cu–Cu^i	2.660 (1)	Cu–O(11)	2.122 (7)
Cu–O(1)	1.958 (5)	Cu–O(6)^i	1.985 (5)
Cu–O(2)^i	1.954 (5)	Cu–O(7)	1.976 (5)
O(1)–C(1)	1.247 (9)	O(6)–C(15)	1.252 (9)
O(2)–C(1)	1.281 (9)	O(7)–C(15)	1.257 (9)
C(1)–C(2)	1.525 (10)	C(15)–C(16)	1.529 (10)

Angles			
Cu^i–Cu–O(1)	83.22 (14)	O(1)–Cu–O(11)	97.21 (24)
Cu^i–Cu–O(2)^i	85.12 (15)	O(2)^i–Cu–O(6)^i	89.33 (20)
Cu^i–Cu–O(6)^i	82.69 (14)	O(2)^i–Cu–O(7)	90.02 (21)
Cu^i–Cu–O(7)	85.47 (15)	O(2)^i–Cu–O(11)	94.45 (25)
Cu^i–Cu–O(11)	177.83 (20)	O(6)^i–Cu–O(7)	168.15 (21)
O(1)–Cu–O(2)^i	168.34 (21)	O(6)^i–Cu–O(11)	95.17 (24)
O(1)–Cu–O(6)^i	89.56 (20)	O(7)–Cu–O(11)	96.67 (24)
O(1)–Cu–O(7)	88.69 (20)		
Cu–O(1)–C(1)	123.7 (5)	Cu–O(7)–C(15)	120.6 (5)
O(1)–C(1)–O(2)	127.0 (7)	O(6)–C(15)–O(7)	127.7 (7)
O(1)–C(1)–C(2)	116.2 (6)	O(6)–C(15)–C(16)	114.9 (6)
O(2)–C(1)–C(2)	116.8 (6)	O(7)–C(15)–C(16)	117.4 (6)
C(1)–C(2)–C(3)	124.2 (7)	C(15)–C(16)–C(17)	125.2 (7)
C(1)–C(2)–C(7)	117.9 (6)	C(15)–C(16)–C(21)	117.1 (6)

[a] Symmetry code: (i) $0.5 - x$; $0.5 - y$; $1.5 - z$.

structure. The infrared spectrum displays stretching values for the carboxylate groups at the expected frequency values (1620 and 1395 cm^{-1}).

CONCLUSIONS

As shown by the results presented here, the pesticide Acifluorfen is an effective ligand toward copper(II). The binding properties of the ligand, which are evidenced by both the solution and the solid-state studies, are mainly those expected for a carboxylic ligand. Carboxylic complexes are formed in dilute solutions, and they are more stable than expected, likely due to the assistance of the nitro group in metal coordination. Rather insoluble complexes having a dimeric structure precipitate from more concentrated solutions.

In soil, while the former behavior (metal ion speciation) is expected to occur in solution, the conditions favoring the precipitation of the metal–pesticide complexes could be met in the phases containing high metal concentrations, i.e., in mineral colloids. Therefore, these
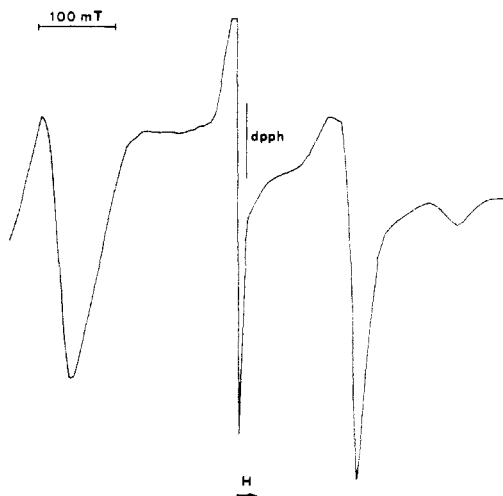
Figure 3. X-band polycrystalline ESR spectrum of the complex $Cu_2(AF)_4(EtOH)_2$.

interactions could be responsible for mutual effects, including immobilization and inactivation, between the pesticide and metal ions in the environment.

Supplementary Material Available: Anisotropic thermal parameters of the non-hydrogen atoms and complete lists of bond distances and angles with their ESD's (5 pages). Ordering information is given on any current masthead page.

LITERATURE CITED

Brown, G. M.; Chidambaram, R. Dinuclear Copper(II) Acetate Monohydrate. A Redetermination of the Structure by Neutron-Diffraction Analysis. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 2393–2403.

Decock, P.; Dubois, B.; Lerivrey, J.; Gessa, C.; Urbanska, J.; Kozlowski, H. Cu(II) Binding by Substituted 1,3,5-Triazine Herbicides. *Inorg. Chim. Acta* **1985**, *107*, 63–66.

De Ford, D. D.; Hume, D. N. The Determination of Consecutive Formation Constants of Complex Ions from Polarographic Data. *J. Am. Chem. Soc.* **1951**, *73*, 5321–5322.

De Meester, S. R.; Fletcher, S. R.; Skapski, A. C. Refined Crystal Structure of Tetra-μ-acetato-bisaquodicopper(II). *J. Chem. Soc., Dalton Trans.* **1973**, 2575–2578.

Hensley, D. L.; Beuerman, D. S. N.; Carpenter, P. L. The Inactivation of Glyphosate by Various Soils and Metal Salts. *Weed Res.* **1978**, *18*, 287–291.

International Tables for X-ray Crystallography; Kynoch: Birmingham, England, 1974; Vol. IV.

Johnson, W. O.; Kollman, G. E.; Swithenbank, C.; Yih, R. Y. RH-6201 (Blazer): A New Broad Spectrum Herbicide for Post-emergence Use in Soybeans. *J. Agric. Food Chem.* **1978**, *26*, 285–286.

Lerivrey, J.; Decock, P.; Dubois, B.; Urbanska, J.; Kozlowski, H. Potentiometric, Spectroscopic and Polarographic Studies on Cu(II)-Prometone-D-Glucosamine Ternary System. *Inorg. Chim. Acta* **1986**, *124*, L11–L13.

Micera, G.; Dessi', A.; Kozlowski, H.; Radomska, B.; Urbanska, J.; Decock, P.; Dubois, B.; Olivier, I. Oxovanadium(IV) and Copper(II) Coordination by D-Galacturonic and D-Glucuronic Acids. *Carbohydr. Res.* **1989**, *188*, 25–34.

Pusino, A.; Gessa, C.; Kozlowski, H. Catalytic Hydrolysis of Quinalphos on Homoionic Clays. *Pestic. Sci.* **1988**, *24*, 1–8.

Sheldrick, G. M. *SHELX-76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

Syntex. *XTL/XTLE Structure Determination System*; Syntex Analytical Instruments: Cupertino, CA, 1976.