PPH (15:85). The yields were lower (about 70%).

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Supplementary Material Available: Table III, listing U_{ij} for all nonhydrogen atoms, Table IV, listing hydrogen atom parameters, Table V, listing the full set of bond distances, and Table VI, listing the full set of bond angles (15 pages); Table VII, listing observed and calculated structure factor amplitudes (×10) for all observed reflections (25 pages). Ordering information is given on any current masthead page.

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Solid-State and Solution Chemistry of Calcium *N*-(Phosphonomethyl)glycinate

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The solid-state and solution chemistry of the calcium salt of *N*-(phosphonomethyl)glycine (glyphosate) has been investigated. The molecular structure of the calcium salt, $CaC_3H_6NO_5P \cdot 2H_2O$, has been determined by single-crystal X-ray diffraction. The structure is polymeric. The calcium atom is seven-coordinate with four oxygen atoms from three different phosphonate groups, one carboxylate oxygen from yet another glyphosate, and two water oxygens. Each glyphosate is in turn bonded to four different calcium atoms through both the phosphonate and carboxylate ends. The nitrogen atom is protonated and therefore does not bind to the calcium. The compound crystallizes in space group $P\bar{1}$ with $Z = 2$ and $a = 5.4336$ (7) Å, $b = 7.9530$ (10) Å, $c = 10.3868$ (9) Å, $\alpha = 74.576$ (8)°, $\beta = 78.495$ (9)°, and $\gamma = 83.044$ (10)°. The final residuals for 159 variables refined against the 1047 data for which $F^2 > 3\sigma(F^2)$ were as follows: agreement $R = 2.09\%$ and $R_w = 3.50\%$. Calcium-selective-electrode titration data were used to determine the stability constant ($\log \beta_{ML} = 3.35$ (1)) and showed no evidence for an ML_2 complex. The solubility product (K_{sp}) and the formation constant (K_1) of calcium glyphosate (CaHL) were determined by analysis of total calcium in a series of saturated solutions of calcium glyphosate dihydrate containing increasing amounts of the dipotassium salt of glyphosate. The values of $\log K_{sp}$ and $\log K_1$ are −5.32 (2) and 2.04 (9), respectively.

Introduction

The introduction of *N*-(phosphonomethyl)glycine (glyphosate) as a commercial herbicide in the 1970s[1] has been described as a revolutionary advance in agriculture.[2] The utility of this compound is based on its unique properties: (1) It is absorbed by all green plant material, is translocated throughout the plant, and then kills the entire plant, including roots or rhizomes. (2) It inhibits a specific plant enzyme and as a result is not toxic to animals. (3) On contact with soil it is immobilized and inactivated, so that it only affects plant material it immediately contacts. (4) In the soil it is degraded within a period of days by soil organisms to CO_2, PO_4^{3-}, and NH_3.

Although complexation certainly must play a role in property 3, relatively little is known about the coordination behavior of this potentially tridentate ligand. A study by Wauchope et al.[3] first examined the acid solution equilibria of glyphosate. Subsequently, Madsen et al.[4] determined the stability constants of the divalent complexes ML^- (M = Cu, Zn, Mn, Ca, and Mg; L = glyphosate trianion) and redetermined the protonation constants. More recently, Motekaitis and Martell[5] redetermined the protonation constants of the glyphosate ligand, redetermined the stability constants for a number of the ML^- species, and examined other divalent as well as trivalent metal ion complexes.

While the structure of the zwitterionic free acid, $HO_2CCH_2NH_2^+CH_2PO_3H^-$, has been determined,[6] no structure determination of a glyphosate complex has been published. The complex calcium salt $Ca(H_2L)_2(H_3L)_2$[7] has been examined. In this salt there are neutral zwitterionic glyphosate molecules and monoanions in which the carboxylate groups are deprotonated. However, the coordination of the Ca^{2+} ions from both glyphosate species is only through phosphonate oxygens. Recently an NMR study of the platinum complexes of glyphosate[8] has presented the first information about the structure of a glyphosate metal complex involving coordination via the nitrogen.

We have prepared the sparingly soluble salt of the glyphosate dianion $CaHL \cdot 2H_2O$ and examined its solid-state structure. We have also determined its solubility product and reinvestigated its solution equilibria (reported to involve the species CaL^-, CaHL, and CaL_2^{4-}).[5] The equilibrium constants reported by Motekaitis and Martell were determined by pH potentiometric titrations on the assumption of a homogeneous solution, and so that study assumed the absence of any solid/solution equilibrium. Furthermore, any equilibrium reaction that does not evolve or consume protons in the pH range studied is relatively insensitive to pH potentiometry. The stability constant ($\log K$) reported by Motekaitis and Martell for the reaction $CaL^- + L^{3-} = CaL_2^{4-}$ is 2.62.[5] Such a low stability constant results in the putative CaL_2^{4-} species being formed only when L^{3-} is the major ligand species, i.e., above the pH of the last protonation constant, 10.142. As seen in the species distribution curve calculated by Motekaitis and Martell (Figure 6 of ref 5), the CaL_2 species becomes significant only above pH 10. Thus, the dominant reaction in the pH range where CaL_2 is reported to be formed does not evolve or consume protons. In the present study direct measurement of calcium concentration, by chemical analysis or a calcium ion selective electrode, has been used to characterize the equilibrium reactions and their thermodynamic constants. We conclude that there is no evidence for a CaL_2^{4-} species. Furthermore, even the glyphosate trianion coordinates to calcium only through the phosphonate group, with little or no involvement of the nitrogen.

Experimental Section

General Considerations. All chemicals were reagent grade. The glyphosate was obtained as the pure crystalline acid (99.9%) from Monsanto. The pH (not $p[H^+]$) was monitored by a Fisher Accumet Model 825 MP pH meter and glass pH electrode, calibrated at pH 7.00 and 10.00. Microanalytical and atomic absorption analyses were performed

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(1) Grossbard, E.; Atkinson, D. *The Herbicide Glyphosate*; Butterworths: London, 1985.
(2) Holly, K. In ref 1, pp 451-453.
(3) Wauchope, D. *J. agric. Food Chem.* **1976**, *24*, 717.
(4) Madsen, H. E. L.; Christensen, H. H.; Gottlieb-Petersen, C. *Acta Chem. Scand., Sect. A* **1978**, *A32*, 79.
(5) Motekaitis, R. J.; Martell, A. E. *J. Coord. Chem.* **1985**, *14*, 139.
(6) Knuuttila, P.; Knuuttila, H. *Acta Chem. Scand., Sect. B* **1979**, *B33*, 623.
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Table I. Crystal, Data Collection, and Refinement Parameters for $CaC_3H_6NO_5P \cdot 2H_2O$

(A) Crystal Parameters at 25 °C[a,b]

a = 5.4336 (7) Å	space group: $P\bar{1}$
b = 7.9530 (10) Å	fw = 243.17
c = 10.3868 (9) Å	Z = 2
α = 74.576 (8)°	d_{calcd} = 1.91 g cm^{-3}
β = 78.495 (9)°	d_{obsd} = 1.91 g cm^{-3} [c]
γ = 83.044 (10)°	μ_{calcd} = 9.17 cm^{-1}
V = 422.9 (1) Å^3	cryst size: 0.10 × 0.11 × 0.45 mm

(B) Data Measurement Parameters[d]

radiation: Mo Kα (λ = 0.709 26 Å)
monochromator: highly oriented graphite (2θ = 12.2°)
detector: cryst scintillation counter, with PHA
rflns measd: $+h,\pm k,\pm l$
2θ range: 3–45°; θ,2θ scans
scan speed: 0.66–6.7° min (θ)
scan width: $\Delta\theta = 0.55 + 0.347 \tan\theta$
bkgd: measd over 0.25($\Delta\theta$) added to each end of the scan
aperture to cryst: 173 mm
vert aperture: 3.0 mm
horiz aperture: 2.0 + 1.0 tan θ mm (variable)
no. of unique rflns collected: 1101
no. of rflns with $F^2 > 3\sigma(F^2)$: 1047
intens stds: (037), (2$\bar{3}$4), (32$\bar{3}$); measd every 1 h of X-ray exposure time; no signif decay obsd
orientation: 3 rflns checked after every 250 measmts; cryst orientation redetermined if any rflns offset from their predicted positions by more than 0.1°; reorientation not necessary during data collection

(C) Solution and Refinement Parameters

soln: direct methods[e]
refinement: full-matrix least squares
hydrogens: all found by difference Fourier and refined with isotropic thermal params
extinction coeff:[f] refined to $g = 1.47 \times 10^{-6}$ e^{-2}
no. of variables: 159
R = 2.09%
R_w = 3.50%
R_{all} = 2.25
GOF = 2.72
p = 0.02
max peak on ΔF map: 0.30 e Å^{-3} near P

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ near 30°. [b] In this and all subsequent tables the esd's of all parameters are given in parentheses. [c] Measured by flotation in CCl_4/CH_2Br_2 mixture. [d] Please see ref 9. [e] Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. "MULTAN 11/82: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York, York, England, and University of Louvain, Louvain, Belgium, 1982. [f] Zachariesen, W. H. *Acta Crystallogr.* **1963**, *18*, 1139.

by the analytical laboratory at the University of California at Berkeley.

Preparation of Calcium Glyphosate Dihydrate. Calcium nitrate tetrahydrate (0.603 g, 2.55 mmol) was added to a glyphosate solution (37.0 mL, 0.0692 M, 2.56 mmol). Absolute ethanol (5 mL) was added, and then a sodium hydroxide solution (≃1 M) was added dropwise until the resulting precipitate would not redissolve upon stirring; one drop of nitric acid (10%) was added, and the precipitate redissolved immediately. Urea (4.1 g, 68 mmol) was added, and the solution was warmed on a hot plate in a loosely covered Erlenmeyer flask overnight. (The slow hydrolysis of urea generates a gradual, homogeneous increase in pH due to the release of ammonia.) The resulting white crystalline solid was collected by filtration, washed with ethanol, and then dried at 80 °C under vacuum for 8 h. Anal. Calcd (found) for $CaC_3H_6NO_5P \cdot 2H_2O$: C, 14.82 (14.92); H, 4.15 (4.34); N, 5.76 (5.69); P, 12.74 (12.68); Ca, 16.5 (15.1, by atomic absorption); O, 46.1 (47.3, by difference).

X-ray Crystallography. A small, clear, colorless, needlelike crystal was cleaved, and the fragment was mounted on a glass fiber. The triclinic crystal system was suggested by preliminary precession photographs, and the space group $P\bar{1}$ was eventually confirmed by the final structure. The cell parameters and specific data collection parameters are given in Table I. The structure determination was carried out by the observation of 1101 unique raw intensity data, which were converted to structure factor amplitudes and their esd's by corrections for scan speed, background, and Lorentz and polarization effects.[9] No correction for crystal decomposition was necessary. Inspection of the azimuthal scan data showed a variation of ±1.5% for the average curve.[10] No correction for absorption was applied. The final residuals[9] for 159 variables refined against the 1047 data for which $F^2 > 3\sigma(F^2)$ were agreement R = 2.09% and R_w = 3.50%. The positional and thermal parameters of the atoms are listed in Table II. Values of F_o and F_c, general temperature factor expressions (B's), and root-mean-square amplitudes of vibration are listed in supplementary Tables S1–S3, respectively.[11]

Table II. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
Ca	−0.15988 (6)	0.29597 (4)	0.62633 (3)	1.159 (8)
P	−0.30138 (8)	0.41300 (6)	0.34223 (4)	1.101 (9)
O1	−0.5372 (2)	0.5015 (2)	0.2892 (1)	1.59 (3)
O2	−0.1689 (2)	0.5202 (2)	0.4052 (1)	1.50 (3)
O3	−0.3377 (2)	0.2347 (2)	0.4403 (1)	1.62 (3)
O4	0.3744 (3)	−0.0402 (2)	0.2673 (1)	2.29 (3)
O5	0.6866 (3)	0.0325 (2)	0.0931 (1)	2.84 (3)
O6	0.1851 (2)	0.1188 (2)	0.5394 (1)	2.16 (3)
O7	−0.0549 (2)	0.2239 (2)	0.8521 (1)	2.11 (3)
N	0.1598 (3)	0.2869 (2)	0.2275 (1)	1.54 (3)
C1	−0.0841 (3)	0.3757 (2)	0.1931 (2)	1.66 (4)
C2	0.3365 (3)	0.2340 (2)	0.1131 (2)	1.86 (4)
C3	0.4797 (4)	0.0593 (2)	0.1638 (2)	1.60 (4)
HNA	0.143 (4)	0.192 (2)	0.289 (2)	2.2 (4)*
HNB	0.247 (4)	0.362 (3)	0.261 (2)	3.8 (5)*
H1A	−0.052 (4)	0.493 (3)	0.122 (2)	2.7 (4)*
H1B	−0.153 (4)	0.299 (3)	0.153 (2)	3.0 (5)*
H2A	0.249 (4)	0.226 (3)	0.048 (2)	2.9 (5)*
H2B	0.444 (4)	0.328 (2)	0.066 (2)	2.3 (4)*
H6A	0.224 (4)	0.025 (2)	0.550 (2)	2.3 (5)*
H6B	0.332 (4)	0.157 (3)	0.520 (2)	2.9 (5)*
H7A	0.081 (4)	0.150 (3)	0.856 (2)	2.9 (5)*
H7B	−0.146 (4)	0.172 (2)	0.913 (2)	2.3 (4)*

[a] Values marked with an asterisk are for atoms refined with isotropic thermal parameters. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Calcium-Selective-Electrode Study. Glyphosate (1.003 g, 5.93 mmol) was dissolved in 50 mL of H_2O, and the pH was raised to 11.01 with NaOH after the addition of KCl (final concentration 0.10 M, 25 °C). The initial total volume was 152.0 mL. The solution was titrated with 0.5-mL increments of $CaCl_2$ solution (0.255 M) with constant stirring while millivolt readings of the calcium ion selective electrode (ISE)[12] were monitored. The pH was monitored and maintained between 10.97 and 11.03 with 0.10 M sodium hydroxide solution (a total of 9.45 mL). The calcium chloride titrant had a background ionic strength of 0.10 M (KCl) and was standardized by an EDTA titration at pH 10 with the ISE. No precipitate was observed after the addition of 40.5 mL of titrant. However, when the mixture stood overnight, a large amount of white precipitate formed in the solution (probably calcium glyphosate, CaHL). The final total volume was 201.9 mL. The ionic strength varied from 0.10 to 0.26. The data were refined by using a modification of the program ORGLS[13] (Oak Ridge General Least Squares). The values of −log [Ca^{2+}] for the refinement were calculated by an iterative routine using the total glyphosate and total calcium concentrations as the independent variables.

Preparation of Solutions for K_{sp} Measurement. A solution of dipotassium glyphosate (0.0167 M) in 0.10 M potassium nitrate[14] was

(9) For details regarding data reduction and processing, scattering factor tables, and the program ORTEP, please refer to: Eigenbrot, C. W., Jr.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2653.
(10) Reflections used for azimuthal scans were located near χ = 90°, and the intensities were measured at 10° increments of rotation of the crystal about the diffraction vector.
(11) Please see the statement at the end of this paper regarding supplementary tables.
(12) The ISE was an Orion Model No. 932000 with reference electrode Model No. 900100. It was calibrated at five points between 1.02×10^{-4} and 7.65×10^{-3} M $CaCl_2$ (0.10 M in KCl), and the least-squares line for conversion from millivolts to −log [Ca^{2+}] had a slope of 25.6 (7) and a y intercept of 88 (2) (r = 0.999).
(13) Busing, W. R.; Levy, H. A. Report ORNL-TM-271; Oak Ridge National Laboratory: Oak Ridge, TN, 1962.

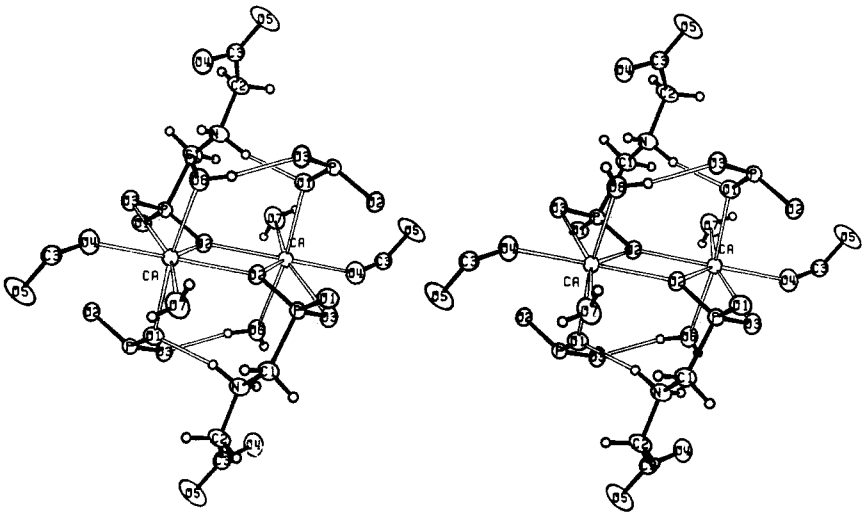

Figure 1. The Ca^{2+} coordination environment. This view shows the coordination environment of the two adjacent calcium ions. The view direction is approximately down the *b*–*c* diagonal, and the horizontal axis runs approximately down the *a*–*b* diagonal. The ellipsoids are scaled to represent the 60% probability surface. Hydrogen atoms, where represented, are given as arbitrarily small spheres for clarity.

prepared (referred to as solution A) by the addition of a standard potassium hydroxide solution to solid glyphosate. Six volumetric flasks (10.0 mL) were prepared with 23–25 mg of calcium glyphosate dihydrate in each. Varying amounts of solution A (see Table IV) were added, and the solutions were diluted with 0.10 M potassium nitrate solution. The solutions were equilibrated in a sonication bath for ≃7 h, cooled over ≃2 h from 35 to 25 °C, and then placed in a 25.0 °C constant-temperature bath (Lauda-Brinkmann, Model K-2/R) for ≃15 h. The solutions were filtered (0.2-μm Acrodisk filter) into vials, the pHs were measured, and the samples were submitted for calcium analysis.

Results and Discussion

Synthesis. The crystalline compound with the formula $Ca(O_3PCH_2NH_2CH_2CO_2)(H_2O)_2$ was prepared by slowly increasing the pH of a water/ethanol mixture containing a 1:1 mixture of glyphosate and calcium nitrate. The pH was raised in situ by adding urea, which upon heating slowly hydrolyzes to form carbon dioxide and ammonia.

Structure. The structure is polymeric. Each calcium atom is bonded to four different glyphosate molecules, and each glyphosate is bonded to four different calcium atoms. A hydrogen-bonding network connects each glyphosate molecule to another glyphosate molecule and each water molecule to a glyphosate molecule. The nitrogen atom is protonated and therefore does not bind to the calcium. The bond distances and angles are listed in Table III.

Figure 1 (Figures 1–3 are ORTEP[9] stereopair drawings) illustrates the numbering scheme and the coordination environment around the two adjacent calcium atoms. An inversion center lies on the midpoint of the line between these two atoms, which are 3.93 Å apart and are bridged by two phosphate oxygens, O2, from two different glyphosate anions. This type of bridging structure is different from that seen in metal (Cu^{2+}, Zn^{2+}, Co^{2+}) complexes of (aminomethyl)phosphonate, where the phosphate bridges two metal atoms via two oxygens from the same phosphate unit as in M–O–P–O–M.[15-17] The metal–metal distance for the copper complex of this sort is 4.94 Å.[15]

Each calcium atom is seven-coordinate with four phosphate oxygens (O1, two O2's, and O3) from three different glyphosates, one carboxylate oxygen (O4) from yet another glyphosate, and two water oxygens (O6 and O7). The coordination polyhedron can be approximated as a pentagonal bipyramid, wherein the pentagon is made up of two O2's, O3, O4, and O7. The distances

Table III. Intermolecular Distances (Å) and Angles (deg)

Ca–O1	2.368 (1)	Ca–O4	2.363 (1)
Ca–O2	2.511 (1)	Ca–O6	2.383 (1)
Ca–O2	2.362 (1)	Ca–O7	2.428 (1)
Ca–O3	2.503 (1)		
P–O1	1.516 (1)	N–C2	1.491 (2)
P–O2	1.518 (1)	C2–C3	1.525 (2)
P–O3	1.519 (1)	C3–O4	1.234 (2)
P–C1	1.820 (1)	C3–O5	1.243 (2)
C1–N	1.487 (2)		
O6–H6A	0.73 (2)	N–HNB	0.97 (2)
O6–H6B	0.86 (2)	C1–H1A	1.04 (2)
O7–H7A	0.89 (2)	C1–H1B	0.97 (2)
O7–H7B	0.77 (2)	C2–H2A	0.92 (2)
N–HNA	0.85 (2)	C2–H2B	0.97 (2)
O1–HNB	1.82 (2)	O1–N	2.778 (1)
O3–H6B	1.92 (2)	O3–O6	2.764 (1)
O5–H7A	1.84 (2)	O5–H7B	2.01 (2)
O5–O7	2.708 (1)	O5–O7	2.764 (1)
O1–Ca–O2	82.76 (3)	O2–Ca–O3	125.31 (3)
O1–Ca–O2	92.00 (3)	O2–Ca–O4	153.33 (3)
O1–Ca–O3	104.24 (3)	C2–Ca–O6	80.40 (4)
O1–Ca–O4	97.99 (3)	O2–Ca–O7	78.42 (3)
O1–Ca–O6	172.39 (4)	O3–Ca–O4	76.02 (3)
O1–Ca–O7	83.78 (3)	O3–Ca–O6	80.66 (3)
O2–Ca–O2	72.49 (3)	O3–Ca–O7	153.78 (3)
O2–Ca–O3	58.82 (3)	O4–Ca–O6	88.79 (4)
O2–Ca–O4	133.16 (3)	O4–Ca–O7	78.17 (4)
O2–Ca–O6	95.12 (3)	O6–Ca–O7	94.32 (4)
O2–Ca–O7	147.36 (3)		
C1–P–O1	104.72 (5)	P–C1–N	111.90 (9)
C1–P–O2	106.63 (5)	C1–N–C2	114.86 (10)
C1–P–O3	106.42 (6)	N–C2–C3	110.63 (11)
O1–P–O2	115.82 (5)	C2–C3–O4	116.55 (11)
O1–P–O3	114.21 (5)	C2–C3–O5	115.66 (12)
O2–P–O3	108.30 (5)	O4–C3–O5	127.76 (12)
C1–N–HNB	110.2 (9)	HNB–O1–P	117.4 (5)
C2–N–HNB	107.6 (9)	HNB–O1–Ca	98.2 (5)
N–HNB–O1	167.0 (14)		
Ca–O6–H6B	118.3 (11)	H6B–O3–P	121.3 (5)
O6–H6B–O3	168.4 (15)	H6B–O3–Ca	106.5 (5)
Ca–O7–H7A	109.7 (10)	H7A–O5–C3	124.4 (5)
O7–H7A–O5	164.5 (15)		
Ca–O7–H7B	119.6 (11)	H7B–O5–C3	130.6 (4)
O7–H7B–O5	166.5 (16)		

(14) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1982; Vol. IV, p 48; *Ibid.* Vol. V, p 418. The formation constants for calcium nitrate and calcium chloride are similar and negligible.
(15) Glowiak, T.; Sawka-Dobrowolska, W.; Jezowska-Trzebiatowska, B.; Antonow, A. *J. Cryst. Mol. Struct.* **1980**, *10*, 1.
(16) Fenot, P.; Darriet, J.; Garrigou-Lagrange, C.; Cassaigne, A. *J. Mol. Struct.* **1978**, *43*, 49.
(17) Glowiak, T.; Sawka-Dobrawolska, W.; Jezowska-Trzebiatowska, B.; Antonow, A. *Inorg. Chim. Acta* **1980**, *45*, L105.

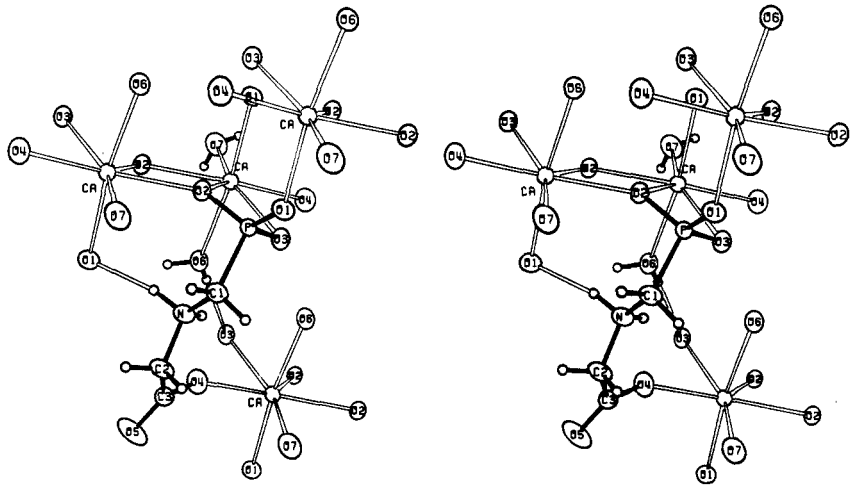

Figure 2. The glyphosate anion environment. This orientation is similar to that in Figure 1 and illustrates a single glyphosate molecule and its bonding to four different calcium atoms.

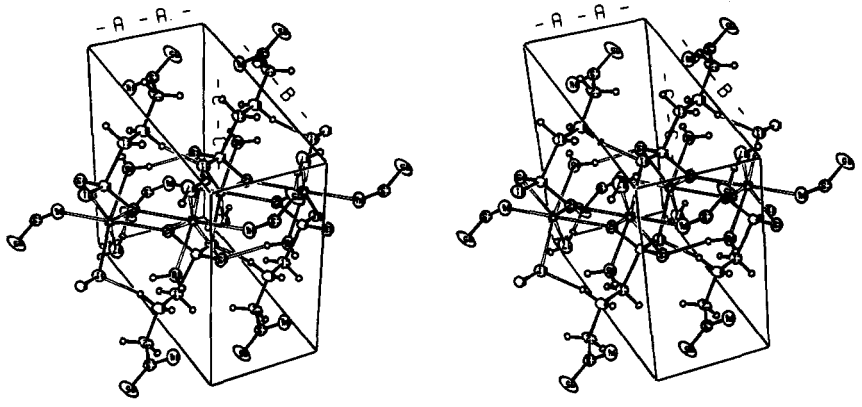

Figure 3. Stereoview of the unit cell packing diagram. This view illustrates the three-dimensional polymeric nature of this material, which is comprised of an infinite network of Ca–O and hydrogen bonds extending in three dimensions.

of these atoms from their corresponding least-squares plane[18] range from 0.005 (1) Å for O4 to −0.374 (1) Å for O2. The calcium atom is −0.068 Å from the plane, and O1 and O6 are −2.411 (1) and 2.313 Å from the plane, respectively. The O1–Ca–O6 angle is 172.39 (4)°, and the pentagon angles range from 58.82 (3) to 78.42 (3)° for O2–Ca–O3 and O2–Ca–O7, respectively. (An ideal pentagonal angle would be 72°.)

Figure 2 illustrates a single glyphosate molecule and how it is bonded to four different calcium atoms: O1 and O3 each bind one calcium atom, and O3 is shared by a calcium atom and a hydrogen bond to O6 (Figure 1); O2 is shared by two different calcium atoms; O1 is shared by a calcium atom and a hydrogen bond to another glyphosate nitrogen. One of the carboxylate oxygens (O4) is bonded to calcium, and the other (O5) is hydrogen-bonded to two different water oxygens (both O7's, Figure 3). The hydrogen bond lengths (O–O or O–N) range from 2.708 (1) to 2.778 (1) Å with angles ranging from 164.5 (15) to 168.4 (15)°.

A comparison of this structure to the structure of glyphosate acid[6] shows that the bond distances and angles are similar; the differences can be attributed to the differences in coordination to the phosphonate and carboxylate groups and the differences in binding to a hydrogen or a calcium ion. In the glyphosate structure two of the three P–O bonds are 1.50 Å and the third (the POH group) is 1.58 Å. In the calcium glyphosate structure all three of the P–O bonds are 1.52 Å. The carboxylate C–O bonds in glyphosate (the COOH group) differ by ≃0.1 Å whereas in the calcium glyphosate structure they differ by only 0.01 Å (COO^-). Also, the carboxylate C–C–O angles in glyphosate (COOH) differ by ≃4.0° whereas they differ by only ≃1.0° in calcium glyphosate (COO^-).

The conformation of the glyphosate molecule in the calcium complex is different in one major respect from that in the structure of the free acid. The torsion angle C1–N–C2–C3 is 74.6 (1)° in the glyphosate structure as compared to 143.0° in the calcium glyphosate structure. In other words, the N–C2 bond is twisted by about 68° in one structure relative to that in the other. Thus, C1 and C3 are approximately anti relative to each other in the calcium glyphosate structure, whereas in the glyphosate structure they are in an approximate gauche conformation. The corresponding angles in the calcium double-salt structure $[Ca(H_2L)_2(H_3L)_2]$[7] are 1.6° for H_3L and 83° for H_2L^-. Figure 3 illustrates the unit cell contents and three-dimensional packing arrangement. The polymeric nature of this material and its hydrogen-bonding network result in a structure that is quite rigid, as illustrated by the small thermal parameters (Table II).

Calcium Complexation in Solution. Figure 4 illustrates the experimental data points of the calcium-selective-electrode titration in comparison to the refined data (curve A) and a curve calculated[19] by using Martell's values[5] ($\log \beta_{ML} = 3.25$, $\log \beta_{ML_2} = 5.87$) for the calcium glyphosate formation constants (curve B). Attempts to refine both β_{ML} and β_{ML_2} simultaneously diverged, indicating that there is no evidence for the ML_2 species. Assuming the absence of an ML_2 species allowed β_{ML} to be refined to a final value of 2.24×10^3 [$\log \beta_{ML} = 3.35$ (1)]. The closeness of the least-squares fit to the experimental data using only β_{ML} confirms that β_{ML_2} is insignificant, and a comparison of the two curves in

(18) The least-squares plane has the equation $0.6546x - 0.6822y - 0.3257z - 4.1531 = 0$, where x, y, and z are the orthogonalized coordinates of the atoms. The orthogonal vector **X** is parallel to a, and **Y** is in the a–b plane along the positive b direction.

(19) Values for the protonation constants from ref 5 were used in the calculations ($\log K = 10.142$, 5.460, 2.229). The value of β_{ML} was the variable parameter.

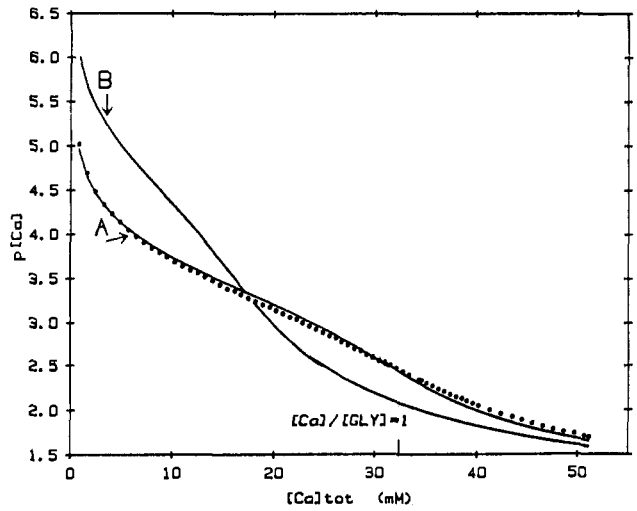

Figure 4. Experimental (dots) and calculated (solid lines) values of $-\log [Ca^{2+}]$, or p[Ca], for the titration of glyphosate with calcium at pH 11.00 (3). The initial and final concentrations of glyphosate are 39 and 29 mM, respectively. The final calcium concentration is 51 mM. Curve A illustrates the least-squares refinement of β_{ML} [refined value of $\log \beta_{ML}$ 3.35 (1)] for calcium glyphosate. Curve B was calculated by using the values $\log \beta_{ML} = 3.25$ and $\log \beta_{ML_2} = 5.87$.[5] If these constants were correct, the CaL_2^{4-} species would account for 93% of the calcium in the early stages of the titration; however, no evidence of this species is seen.

Table IV. Solution Parameters for Measurement of K_{sp} and K_1 for CaHL

soln no.	vol of soln A, mL	pH	$[Ca^{2+}]_{tot}$, mM	$[L]_{tot}$, mM	$[HL^{2-}]$, mM
1	0.00	7.19	2.67	2.67	2.12
2	0.50	7.35	2.43	3.26	2.66
3	1.00	7.39	2.10	3.77	3.17
4	3.00	8.00	1.40	6.40	5.76
5	6.00	7.62	0.963	11.0	10.3
6	10.00	7.78	0.758	17.4	16.8

Figure 4 (A and B) to the experimental curve substantiates this conclusion.

In order to determine the solubility product (K_{sp}) and the formation constant (K_1) of calcium glyphosate (CaHL), a series of saturated solutions of calcium glyphosate dihydrate in 0.10 M potassium nitrate containing increasing amounts of the dipotassium salt of glyphosate were prepared. The following equation can be derived by using the assumption that the total calcium concentration is determined by the free Ca^{2+} and the CaHL complex:

$$[Ca]_{tot} = K_{sp}/[HL^{2-}] + K_1K_{sp}$$

$$K_1 = [CaHL]/[Ca^{2+}][HL^{2-}] \qquad K_{sp} = [Ca^{2+}][HL^{2-}]$$

A plot of $[Ca]_{tot}$ versus $[HL^{2-}]^{-1}$ will be a straight line with a slope of K_{sp} and an intercept of K_1K_{sp}. The calcium ion concentration was measured by atomic absorption, and the pH of the solution was measured in order to determine the HL^{2-} concentration. The HL^{2-} concentrations (Table IV), K_{sp}, and K_1 were calculated by using the calcium glyphosate formation constants and acid dissociation constants of Martell and Motekaitis[5] (The $\log \beta_{MLH}$ value of 11.48 was used as a starting point for the calculation of the HL^{2-} concentration) with the program REFSPEC.[20]

A plot of $[Ca]_{tot}$ versus $[HL^{2-}]^{-1}$ is illustrated in Figure 5 as well as the calculated line (least-squares fit, $r = 0.995$, slope 4.8 (2) $\times 10^{-6}$, y intercept 5.2 (8) $\times 10^{-4}$). The values of $\log K_{sp}$ and $\log K_1$ are -5.32 (2) and 2.04 (9), respectively. This value of K_1 corresponds to a $\log \beta_{MLH}$ value of 12.18 (9).

The mode of coordination of glyphosate to Ca^{2+} in the CaHL and CaL^- species can be deduced from the equilibrium constants and comparison with similar ligands. From potentiometric and NMR data[8] it is clear that the protonation constants of $10^{10.142}$ and $10^{5.460}$ are due to protonation of the glyphosate amine and phosphonate groups, respectively. Since the CaL^- complex forms only upon phosphonate deprotonation, the coordination to Ca^{2+} must involve the $-PO_3^{2-}$ group. This is supported by the similarity of the formation constant determined here to those of the corresponding alkylphosphonates illustrated below for the reaction $Ca^{2+} + RPO_3^{2-} = Ca(O_3PR)$ (the corresponding association constants for carboxylates are much smaller):

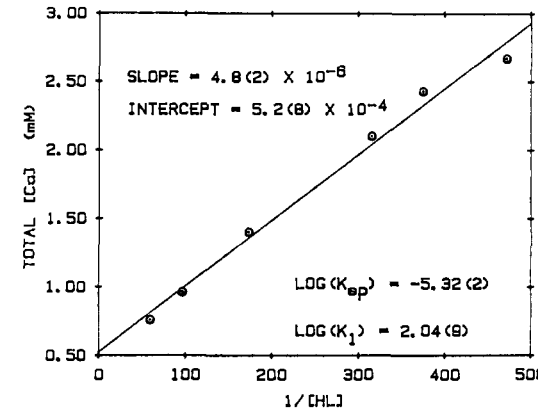

Figure 5. Plot of $[Ca]_{tot}$ versus $[HL^{2-}]^{-1}$ and the least-squares line through the data points.

R group	$\log K_{ML}$	ref
$-CH_3$	1.51	14, Vol. V, p 333
$-CH_2NH_2$	1.71	14, Vol. V, p 264
$-CH_2CH_2NH_2$	1.74	14, Vol. V, p 267
$-CH_2N^+(CH_3)_3$	0.93	14, Vol. V, p 283
$-CH_2CH_2CH_2CH_2PO_3H_2$	2.54	14, Vol. III, p 179
$-CH_2OH$	1.68	14, Vol. V, p 335

The effect that calcium binding has on the amine protonation is also informative; $\log K$ changes from 10.142 for L^{3-} to 8.83 for the protonation of CaL^-. This difference is similar to the difference observed in the $\log K_a$'s of substituted carboxylic acids when the charge is increased by 2 units by changing the functional group on the α-carbon from a carboxylate to an ammonium ion ($\log K_a = 5.69$ and 2.31, respectively).[21] The equations are illustrated below for comparison:

reacn	$\log K_a$	atom protonated
$L^{3-} + H^+ = HL^{2-}$	10.142	N
$CaL^- + H^+ = CaHL$	8.83	N
$^-O_2CCH_2CO_2^- + H^+ = {}^-O_2CCH_2CO_2H$	5.69	O ($-CO_2$)
$H_3N^+CH_2CO_2^- + H^+ = H_3N^+CH_2CO_2H$	2.31	O ($-CO_2$)

These comparisons show that *the amine group does not coordinate significantly to the calcium ion* in the CaL^- complex as well as in the neutral CaHL complex. Furthermore, additional complexation by the carboxylate requires formation of a polymer or a monomeric eight-membered chelate ring. The former is ruled out by the solution equilibria data, and the latter is highly improbable. Therefore, only coordination by the phosphonate group of glyphosate is significant in the calcium complex in solution.

Conclusions

The ability of glyphosate to bind calcium ions at both ends of the molecule and its inability to use the nitrogen as a donor atom favor the formation of the observed, saltlike, polymeric structure in the solid.

The titration of glyphosate with calcium while the free calcium concentration is monitored has allowed the determination of the formation constant of the 1:1 calcium glyphosate complex in solution. We find no evidence for the 1:2 calcium glyphosate species. The use of the calcium ion selective electrode is a much more direct measure of the equilibrium in this case than poten-

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(21) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row: New York, 1981; p 274, Table 3.10.

ɔmetric pH data. Since the proposed reaction[5] $CaL^- + L^{3-} = CaL_2^{4-}$ corresponds to no change in the proton stoichiometry, there is little to distinguish it from the simple deprotonation reaction of glyphosate. In contrast, direct measurement of $[Ca^{2+}]$ allows an evaluation of complex formation that is independent of the protonation reactions.

Similarly, measurement of total calcium by atomic absorption allows a direct evaluation of CaHL equilibria. The value of log β_{MLH} determined by Martell and Motekaitis[5] is 11.48, compared to the value of 12.18 (9) determined in this study. On the basis of the equilibrium constants determined here and the conditions used by Martell and Motekaitis,[5] K_{sp} may have been exceeded in the earlier potentiometric titration experiments; this would account for their lower value for this formation constant.

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Registry No. $Ca(O_3PCH_2NH_2CH_2CO_2)(H_2O)_2$, 112740-48-4; $K_2C_3H_6NO_5P$, 69200-57-3.

Supplementary Material Available: Listings of general temperature factor expressions (B's) and root-mean-square amplitudes of vibration (Tables S2 and S3) (1 page); a listing of observed and calculated structure factors (Table S1) (6 pages). Ordering information is given on any current masthead page.

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Isolation and Characterization of the Principal Kinetic Products in the Rothemund Synthesis of Sterically Hindered Tetraarylporphyrins. Crystal and Molecular Structures of [Tetrakis(2,6-dichlorophenyl)porphinato]zinc(II) and Bis[(*meso*-2,6-dichlorophenyl)-5-(*o*,*o*'-dichlorobenzyl)dipyrromethene]zinc(II) Complexes

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The Rothemund condensation reaction, the most useful route to hindered 5,10,15,20-tetraarylporphyrins, has been examined in detail in context with the production of tetrakis(2,6-dichlorophenyl)porphyrin, TDCPP, a porphyrin used extensively at present in homogeneous oxygenation and biomimetic heme studies. The principal products from the reaction of pyrrole, 2,6-dichlorobenzaldehyde, and zinc acetate in refluxing 2,4,6-collidine are the bis(dipyrromethene) complex bis[(*meso*-2,6-dichlorophenyl)-5-(*o*,*o*'-dichlorobenzyl)dipyrromethene]zinc(II) (**2**), produced in ca. 40% yield, and the Zn porphyrin [tetrakis(2,6-dichlorophenyl)porphinato]zinc(II), Zn^{II}TDCPP (**1**), produced in ca. 10% yield. In contrast to a previous report, there is no evidence that *meso*,5,5'-trisubstituted dipyrromethenes are formed. Furthermore, no zinc complexes of pyrromethenes nor dipyrromethanes build up to observable levels under the conditions of this aerobic high-temperature condensation reaction. The X-ray crystal structure of **2** coupled with ^{1}H NMR, ^{13}C NMR, infrared, UV–visible, and mass spectral data confirms the formulation of the compound as a Zn^{2+} ion coordinated by two planar bidentate disubstituted dipyrromethene ligands. Although the data indicate that carbon–carbon bond formation and cyclization in **2** to form the metalloporphyrin, **1**, should not be a difficult process, **2** does not produce **1** in appreciable yield under the Rothemund conditions examined in this work. The metalloporphyrin, **1**, isolated from the reaction, crystallizes as its five-coordinate *N*-methylpyrrolidinone (NMP) complex in triclinic space group $P\bar{1}$: a = 11.470 (9) Å, b = 13.155 (7) Å, c = 19.894 (10) Å, α = 84.25 (4)°, β = 79.00 (5)°, γ = 75.59 (6)°; V = 2849.3 (3.3) Å^3, Z = 2. The zwitterionic canonical form of the O-bound axial NMP is considerably enhanced upon ligation to the zinc, and the pocket depth defined by the eight phenyl *o*-chloro substituents in **1** is ca. 2.6 Å. Although the spectroscopic data indicate that free-radical bromination of **2** followed by treatment of the product under Rothemund condensation conditions yields some porphyrin, the principal products are brominated derivatives of **1** and **2**.

Introduction

Few areas in chemical research has been as active since 1980 as the use of synthetic transition-metal porphyrins to model the electronic and reactivity features of cytochrome P-450 and to catalyze the oxidation of hydrocarbons and other organic substrates.[1-15] The most recent work has largely focused on the use of 5,10,15,20-tetraarylmetalloporphyrins with bulky substituents on the ortho positions of the aryl rings. These sterically hindered

(1) Recent reviews of cytochrome P-450: (a) White, R. E.; Coon, M. J. *Annu. Rev. Biochem.* **1980**, *49*, 315. (b) Guengerich, F. P.; MacDonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9. (c) *Cytochrome P-450*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986.

(2) References 3–15 involve the use of metallotetraarylporphyrin complexes with bulky ortho substituents on the aryl rings. Many of the studies involve modeling the electronic and reactivity features of cytochrome P-450 by synthetic metalloporphyrins. Papers are listed alphabetically by the principal investigator's last name.

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