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The complex chemistry of *N*-(phosphonomethyl)glycine (glyphosate): preparation and characterization of the ammonium, lithium, sodium (4 polymorphs) and silver(I) complexes

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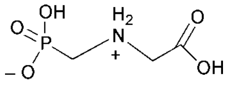
A series of complexes with the herbicide glyphosate [*N*-(phosphonomethyl)glycine = H_3L] has been synthesized and characterized using infrared spectroscopy, and in the case of five of these, by single crystal X-ray diffraction. The compounds are ammonium glyphosate $[NH_4][H_2L]$ **1**, lithium glyphosate $Li(H_2L)$ **2**, sodium glyphosate hemi-hydrate $Na(H_2L)\cdot 0.5H_2O$ **3**, sodium glyphosate monohydrate $Na(H_2L)\cdot H_2O$ **4**, sodium glyphosate dihydrate $Na(H_2L)\cdot 2H_2O$ **5**, disodium glyphosate nonahydrate $Na_2(HL)\cdot 9H_2O$ **6** and disilver glyphosate $Ag_2(HL)$ **7**. The crystal structures of **1**, **3**, **4**, **6** and **7** have been determined. Compound **1** consists of a hydrogen-bonded lattice structure in which all of the available ammonium protons are involved in hydrogen bonding, together with the zwitterionic amine group and the single phosphonate proton. Compounds **3** and **4** are both polymeric and based on dimeric repeating units with six-co-ordinate sodium centres. Complex **6** is based on both discrete octahedral $[Na(HL)(H_2O)_5]^-$ anionic complex units with the unidentate glyphosate ligand bonded *via* a carboxylate oxygen, together with a cationic $[Na_2(H_2O)_8]^{2+}$ ribbon polymer. All structures have extensive hydrogen bonding interactions. The silver complex **7** is a polymer structure which involves the phosphonate ligands in linear chains joined through the carboxyl group at one end (*via* bis-*O*,*O′* bridged silver dimers) and silver co-ordinated phosphonate oxygens at the other.

Introduction

Glyphosate is the common name for *N*-(phosphonomethyl)glycine, a total-kill herbicide (introduced in 1974 by the Monsanto Company under the trade name "Roundup"), having the environmental advantages of low mammalian toxicity and rapid breakdown in the soil leaving no harmful residues.[1–3] The crystal structure of this compound shows that it exists in the zwitterionic form with a phosphonate proton delocalized on the amino nitrogen.[4] As a ligand for metal complexation, the glyphosate molecule (H_3L) possesses three internal donor sites [O_p (phosphate), O_c (carboxylate), N (amino)], with potential for formation of both bidentate and tridentate co-ordination *via* 5-membered chelate rings, and additionally for polymer association through the peripheral carboxylate and phosphonate groups.



Glyphosate

Acid dissociation constants[5] [$pK_{a1} = 2.32$ (carboxylate); $pK_{a2} = 5.86$ (phosphonate); $pK_{a3} = 10.86$ (amino), or the redetermined values 2.23, 5.36, 10.14[6]] also suggest a range of possible co-ordination modes. The stability constants for a number of divalent (Cu, Zn, Mn, Ca, Mg) complexes with the trianion (L) were reported in 1978[7] while a series of square planar complexes with platinum(II) were characterized by NMR spectroscopy.[8] The platinum compounds formed over a pH range of 1.5–11, with mixed ligands (NH_3, Cl, H_2O), together with glyphosate in unidentate, bidentate and tridentate co-ordination modes. The first complex characterized by X-ray methods was the relatively insoluble compound with calcium, $\{[Ca(HL)(H_2O)_2]_2\}_n$ ($K_{sp} = 5 \times 10^{-6}$), in which the seven-co-ordinate distorted pentagonal bipyramidal calcium centres comprising the centrosymmetric dimeric repeating unit in the polymeric structure are bound to four different HL ligands and two waters.[9,10] The barium complex with the same basic formula $\{[Ba(HL)(H_2O)_2]_2\}_n$ is also polymeric[11] but the barium centres are eight-co-ordinate and the centrosymmetric dimer is bridged by two HL ligands (O_p and O_c). The strontium analogue was also confirmed to be isostructural with the barium complex. However, in the copper(II) complex,[12] $\{Na[Cu(L)]\cdot 3.5H_2O\}_n$, based on distorted square pyramidal copper centres, the glyphosate ligand is both trianionic and tridentate and occupies meridional co-ordination sites. The polymeric structure is extended *via* bridging through phosphonate oxygens while inter-complex links are formed through phosphonate and carboxylate oxygens to the sodium centres and their co-ordinated waters. The only crystallographically characterized example of a bis-tridentate glyphosate complex is the discretely monomeric $Na_3[Co(L)_2]\cdot 11H_2O$, in which the ligands occupy *trans*-facial octahedral co-ordination sites.[13]

A series of octahedral complexes with dimethylplatinum(IV) complete the known examples.[14] With two of these, $\{Ag[Pt(CH_3)_2(HL)Br]\}_n$ and $Ag_3[Pt(CH_3)_2(HL)Br][Pt(CH_3)_2(L)Br]\cdot 1.5H_2O$, crystallization was facilitated by the presence of AgBr, which was subsequently incorporated in the polymeric structures. A third complex, $[Pt(CH_3)_2(HL)(H_2O)]\cdot H_2O$, is monomeric.

In a program of investigation of the complex chemistry of glyphosate, the ammonium salt of glyphosate, $[NH_4][H_2L]$ **1**, the Group 1 complexes with lithium, $Li(H_2L)$ **2**, and sodium {four polymorphs, $Na(H_2L)\cdot 0.5H_2O$ **3**, $Na(H_2L)\cdot H_2O$ **4**, $Na(H_2L)\cdot 2H_2O$ **5** and $Na_2(HL)\cdot 9H_2O$ **6**} have been prepared

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and characterized. The silver(I) complex $Ag_2(HL)$ **7** has also been prepared and the crystal structures of compounds **1**, **3**, **4**, **6** and **7** have been determined by X-ray diffraction, although that for **7** is considered crystallographically to be of low precision. The summary results from the crystal structure determinations of three polymorphs of sodium glyphosate have been reported by Franz *et al.*[2] in work completed within the Monsanto Company[15] but these remain unpublished. The compounds reported were the dihydrate $Na(H_2L)\cdot 2H_2O$ (assumed to be equivalent to **5** but subsequently proved in this work to be our monohydrate **4**), the nonahydrate $Na_2(HL)\cdot 9H_2O$ (identical with our **6**), and a mixed valence tetrahydrate with formula $Na_3(HL)(H_2L)\cdot 4H_2O$ (not isolated by us). Since no general structural data and crystal packing information were available for these compounds, we determined the structures and in addition completed a comprehensive infrared spectroscopic analysis which has allowed a number of previous anomalies from the literature to be clarified.

Experimental

Preparations

All compounds were prepared from commercial grade glyphosate (Monsanto Chemicals) which was purified by recrystallization from an aqueous solution (*ca.* 25 g dm^{-3}) after boiling for 5 min with 1 g of activated charcoal. The white microcrystalline product had the literature mp (230 °C, decomp.).

$[NH_4][H_2L]$ 1. This was prepared by the slow addition of concentrated ammonia solution to a stirred suspension of 1.69 g (0.010 mol) of glyphosate in 25 cm^3 of water at room temperature until all the solid had dissolved. The solution was filtered and allowed to evaporate at room temperature for 5 days, providing needle-like crystals suitable for X-ray analysis. Yield 1.41 g (76%). Found: C, 19.2; H, 6.0; N, 15.0%. $C_3H_{11}N_2O_5P$ requires C, 19.2; H, 6.0; N, 14.8%.

$Li(H_2L)$ 2. Lithium hydroxide [0.325 g (0.0125 mol)] in 20 cm^3 of water was added dropwise to a stirred solution of glyphosate [2.1 g (0.0124 mol)] in 200 cm^3 of water at 90 °C. Stirring was continued for 15 min after which the solution was evaporated under vacuum to *ca.* 40 cm^3. Cooling to 0–4 °C yielded a small amount of unchanged glyphosate after 2 days. This was removed and ethanol added until a faint turbidity appeared, subsequently removed by dropwise addition of water. Further evaporation at 0–4 °C gave colourless micro-crystals of compound **2**. Yield 0.08 g (22%). Found: C, 20.6; H, 4.7; N, 8.0%. $C_3H_7LiNO_5P$ requires C, 20.6; H, 4.0; N, 8.0%.

$Na(H_2L)\cdot 0.5H_2O$ 3 and $Na(H_2L)\cdot H_2O$ 4. To a stirred solution of glyphosate [3.2 g (0.019 mol)] in 40 cm^3 of water was added 0.75 g (0.0188 mol) of solid NaOH pellets. After stirring for 2 h the solution was filtered to remove traces of undissolved solid, after which ethanol was added until a faint turbidity appeared (*ca.* 20 cm^3). Cooling to 0–4 °C and allowing to stand gave a small quantity of glyphosate after 2 days. Further addition of 10 cm^3 of ethanol and allowing evaporation at 0–4 °C gave well formed colourless crystals of the monohydrate **4**, suitable for X-ray analysis. Yield 0.336 g (9.0%). Found: C, 17.2; H, 4.4; N, 6.4%. $C_3H_9NNaO_6P$ requires C, 17.2; H, 4.3; N, 6.7%. Addition of 10 cm^3 of ethanol to the filtrate and evaporation of the solution gave more crystals of **4** together with a surface deposition of smaller well formed but morphologically different crystals of the hemi-hydrate **3** which were separated physically. Found: C, 18.3; H, 4.2; N, 7.3%. $C_6H_{16}N_2Na_2O_{11}P_2$ (the dimer formula) requires C, 18.0; H, 4.0; N, 7.0%.

$Na(H_2L)\cdot 2H_2O$ 5 and $Na_2(HL)\cdot 9H_2O$ 6. To a stirred solution of 2.01 g (0.012 mol) of glyphosate in 50 cm^3 of water at room temperature were added 2.0 cm^3 of isopropylamine. After all solid had dissolved, 10 cm^3 of a solution containing 2.1 g (0.036 mol) of NaCl were added dropwise. Stirring was continued for 3 h, after which ethanol was added until the solution turned faintly cloudy. It was allowed to evaporate at *ca.* 0–4 °C for 2 weeks. Colourless crystals of the nonahydrate **6**, suitable for X-ray analysis, were formed. Yield 0.585 g (13%). Found: C, 9.5; H, 6.5; N, 3.8%. $C_3H_{24}NNa_2O_{14}P$ requires C, 9.6; H, 6.4; N, 3.7%. Ethanol was subsequently added to the filtrate from the formation of **6** until it turned cloudy and after filtration the solution was allowed to evaporate at 0–4 °C for *ca.* 1 week. Colourless micro-crystals of the dihydrate **5** were obtained. Yield 0.200 g (8.9%). Found: C, 15.8; H, 4.8; N, 5.8%. $C_3H_{11}NNaO_7P$ requires C, 15.9; H, 4.9; N, 6.2%.

$Ag_2(HL)$ 7. To a stirred solution containing 2.01 g (0.012 mol) of silver nitrate in 25 cm^3 of water were added 2.01 g (0.012 mol) of glyphosate at room temperature. Concentrated ammonia solution (28% w/v) was added dropwise until the precipitate which formed redissolved. The solution was stirred for 5 h, then allowed to evaporate at ambient temperature in the dark, providing hard pale brown crystal masses after *ca.* 2 weeks. Yield 1.47 g (32%). Found: C, 9.0; H, 1.6; N, 4.7%. $C_3H_6Ag_2NO_5P$ requires C, 9.4; H, 1.6; N, 3.7%.

Infrared spectra were recorded for all samples as pressed disks in KBr, on a Perkin-Elmer 1600 Fourier-transform infrared spectrometer.

Crystallography

Crystal data. *Compound 1.* $NH_4^+C_3H_7NO_5P^-$, $M = 186.1$, monoclinic, space group $P2_1/c$ (no. 12), $a = 5.1224(9)$, $b = 17.356(2)$, $c = 8.934(1)$ Å, $\beta = 100.53(1)°$, $U = 780.9(2)$ Å^3, $T = 297(2)$ K, $Z = 4$, $D_c = 1.583$ g cm^{-3}, μ(Mo-Kα) = 3.34 cm^{-1}, 2584 reflections measured, 2353 unique ($R_{int} = 0.033$), final $R = 0.039$ (F), $R_w = 0.050$ (F) [1405 observed with $I > 2.0\sigma(I)$].

Compound 3. $(C_3H_7NNaO_5P)_2\cdot H_2O$, $M = 400.1$, monoclinic, space group $P2_1/c$ (no. 12), $a = 15.185(1)$, $b = 9.288(2)$, $c = 10.794(1)$ Å, $\beta = 93.428(7)°$, $U = 1519.6(4)$ Å^3, $T = 293(2)$ K, $Z = 4$, $D_c = 1.749$ g cm^{-3}, μ(Mo-Kα) = 4.00 cm^{-1}, 2817 reflections measured, 2660 unique ($R_{int} = 0.010$), final $R = 0.026$ (F), $wR = 0.067$ (F^2) [2376 observed with $I > 2.0\sigma(I)$].

Compound 4. $C_3H_7NNaO_5P\cdot H_2O$, $M = 209.1$, monoclinic, space group $P2_1/c$ (no. 12), $a = 7.1210(4)$, $b = 11.2074(7)$, $c = 9.6687(8)$ Å, $\beta = 98.602(6)°$, $U = 762.96(9)$ Å^3, $T = 293(2)$ K, $Z = 4$, $D_c = 1.820$ g cm^{-3}, μ(Mo-Kα) = 4.09 cm^{-1}, 1453 reflections measured, 1340 unique ($R_{int} = 0.014$), final $R = 0.023$ (F), $wR = 0.061$ (F^2) [1311 observed with $I > 2.0\sigma(I)$].

Compound 6. $C_3H_6NNa_2O_5P\cdot 9H_2O$, $M = 375.2$, monoclinic, space group $P2_1$ (no. 10), $a = 6.365(1)$, $b = 7.186(2)$, $c = 17.816(3)$ Å, $\beta = 94.04(1)°$, $U = 812.9(3)$ Å^3, $T = 293(2)$ K, $Z = 2$, $D_c = 1.533$ g cm^{-3}, μ(Mo-Kα) = 2.87 cm^{-1}, 1712 reflections measured, 1564 unique ($R_{int} = 0.013$), final $R = 0.024$ (F), $wR = 0.062$ (F^2) [1464 observed with $I > 2.0\sigma(I)$].

Compound 7. $C_3H_6Ag_2NO_5P$, $M = 382.8$, triclinic, space group $P\bar{1}$ (no. 2), $a = 5.400(2)$, $b = 17.168(3)$, $c = 5.010(2)$ Å, $\alpha = 94.49(2)$, $\beta = 115.75(2)$, $\gamma = 81.95(2)°$, $U = 414.2(2)$ Å^3, $T = 293(2)$ K, $Z = 2$, $D_c = 3.069$ g cm^{-3}, μ(Mo-Kα) = 48.9 cm^{-1}, 2100 reflections measured, 1902 unique ($R_{int} = 0.020$), final $R = 0.139$ (F), $R_w = 0.153$ (F) [1297 observed with $I > 3.0\sigma(I)$].

Data collection, structure solution and refinement. X-Ray diffraction data for compounds **1**, **3**, **4**, **6** and **7** were collected at ambient temperature on Rigaku AFC 7R (**1** and **7**) and Enraf-Nonius CAD-4 (**3**, **4** and **6**) four-circle diffractometers (Mo-Kα X-radiation, $\lambda = 0.71069$ Å). Data were corrected for Lorentz and polarization effects, for extinction and for absorption [semi-empirical methods (psi scans) for **1** and **7**, with **3**, **4**, and **6** uncorrected]. The structures were solved by direct methods (SHELXL 97[16] or SIR 92[17]) and refined (on F or F^2) by full-

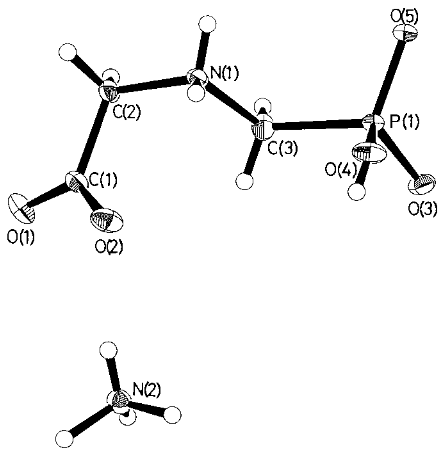


Fig. 1 Molecular conformation and atom numbering scheme for the glyphosate anion in compound **1**.

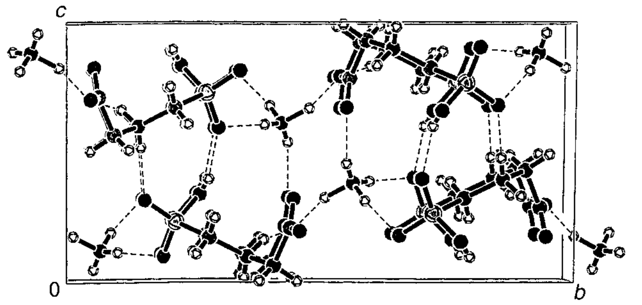


Fig. 2 Packing of compound **1** in the unit cell viewed down *a*. Hydrogen bonding interactions are shown as broken lines.

matrix least squares (SHELXL 97[16] or TEXSAN[18]), with anisotropic thermal parameters for all non-hydrogen atoms giving residuals R and R_w (on F) for **1** and **7** or R and wR (on F^2) for **3**, **4** and **6**. Hydrogen atoms were either located by difference methods or included in the respective refinements at calculated positions as riding models. Selected bond distances and angles for compounds **3**, **4** and **6** are given in Table 1. The atom numbering scheme for the glyphosate residue is as shown in Fig. 1 (compound **1**) and 3 to 5 (**3**, **4** and **6**). Although X-ray data were collected for the silver compound **7**, the structure was not satisfactorily refined ($R = 0.14$), indicating a problem with crystal twinning, which is common with this compound. However, a partial structure is presented, and is considered of sufficient precision to allow an adequate interpretation of the basic molecular structure.

CCDC reference number 186/2123.

See http://www.rsc.org/suppdata/dt/b0/b002748k/ for crystallographic files in .cif format.

Discussion

The structure of ammonium glyphosate, $[NH_4][H_2L]$ **1**, shows discrete ammonium cations and glyphosate(1−) anions, interlinked by a network of hydrogen bonds (Fig. 2). These involve all protons of the ammonium ion and all potential hydrogen bonding sites on the glyphosate functional groups (Table 2). Ion formation proceeds *via* proton transfer from the carboxylate group to the ammonia molecule, with subsequent hydrogen bonding both to two phosphonate oxygens [N(2)···O(3), 2.887(4); N(2)···O(5), 2.918(4) Å] and to two carboxylate oxygens [N(2)···O(1), 2.778(4); N(2)···O(2), 3.014(4) Å]. The two amine protons are associated with both a carboxylate oxygen [N(1)···O(1), 2.82 Å] and a phosphonate oxygen [N(1)···O(3), 2.722(3) Å]. Finally, the single phosphonate proton is linearly associated with a carboxyl oxygen [O(1)···O(3), 2.531(3) Å].

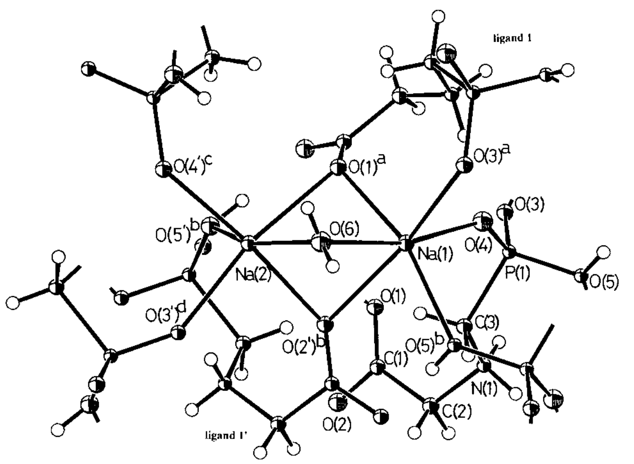


Fig. 3 Molecular configuration and atom numbering scheme within the dimeric repeating unit in compound **3**.

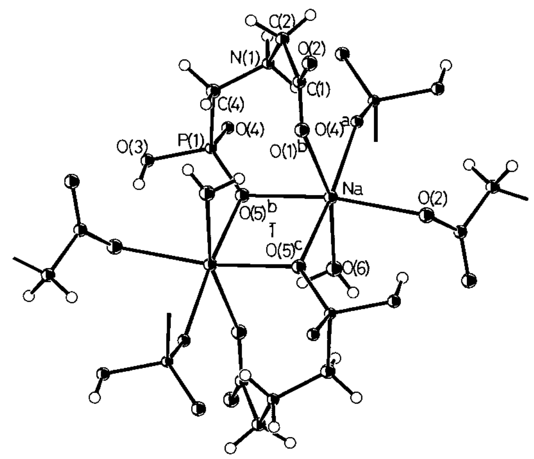
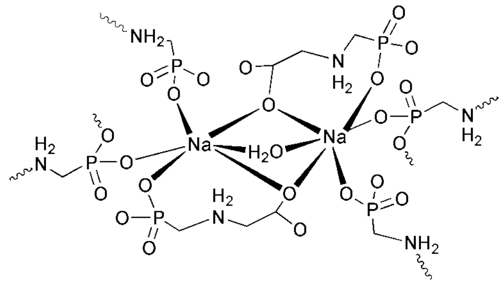


Fig. 4 Molecular configuration and atom numbering scheme within the dimeric repeating unit in compound **4**.



$[\{Na_2(HL)_2(H_2O)\}_n]$

Sodium glyphosate hemihydrate, $[Na_2(HL)_2{\cdot}0.5H_2O]_n$ **3** is polymeric and based on a tris-oxo bridged dimer repeating unit (Fig. 3). The three bridging oxygens are from the single water molecule [Na(1)–O(6), 2.349(2); Na(2)–O(6), 2.381(2) Å; Na–O–Na, 86.68(5)°], and two carboxyl oxygens from two different glyphosate ligands [Na(1)–O(1)^a, 2.344(2); Na(1)–O(2′)^b, 2.583(2) Å; Na(2)–O(1)^a, 2.534(2); Na(2)–O(2′)^b, 2.409(2) Å. These same ligands form open linkages to respective sodium centres [Na(1)–O(3)^a, 2.432(2) and Na(2)–O(5′)^b, 2.497(2) Å]. The Na(1)···Na(2) distance is 3.246(1) Å. The remaining sites in the distorted octahedral co-ordination about both Na(1) and Na(2) are occupied by the oxygens of bridging phosphonate groups [Na(1)–O(4), 2.361(2); Na(1)–O(5)^b, 2.401(2); Na(2)–O(3′)^d, 2.359(2); Na(2)–O(4′)^c, 2.358(2) Å]. The mean Na–O bond length is 2.417 Å over the two co-ordination centres. The protonated amino nitrogen, as expected is not involved in

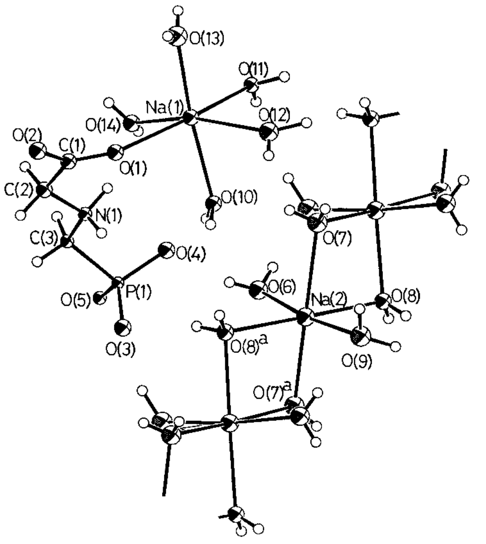
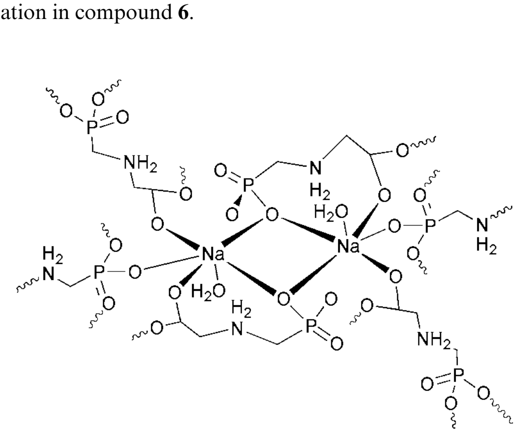


Fig. 5 Molecular configuration and atom numbering scheme for the $[Na(HL)(H_2O)_5]^-$ anion units together with the $[Na_2(H_2O)_8]_n^{2n+}$ polymer cation in compound **6**.



$[\{Na_2(HL)_2(H_2O)_2\}_n]$

co-ordination. Hydrogen-bonding interactions stabilize the structure (Table 2).

Sodium glyphosate monohydrate **4** is also a polymer structure but based upon a centrosymmetric bis-oxo bridged dimeric repeating unit $[Na_2(HL)_2(H_2O)_2]$ (Fig. 4). However, in contrast to the case found in the polymorph **3**, each six-co-ordinate octahedral sodium centre in the dimer is bridged by oxygens from two independent phosphonate groups [Na–O(5)^b, 2.374(1); Na–O(5)^c, 2.389(1) Å; Na–O–Na, 90.71(4)°; Na···Na, 3.389(1) Å]. The co-ordination is completed by a single water oxygen [Na–O(6), 2.586(2) Å], the second (bridging) phosphonate oxygen [Na–O(4)^a, 2.367(1) Å] and two carboxyl oxygens [Na–O(1)^b, 2.378(1); Na–O(2), 2.474(1) Å], both also bridging. The mean Na–O bond distance is 2.426 Å. As found in the other complexes reported here, the glyphosate ligand is zwitterionic. Hydrogen-bonding interactions are present (Table 2).

It should be noted that compound **4** has the same crystal data, including density, as the "dihydrate, $Na(HL)\cdot 2H_2O$" from ref. 2 [$a = 7.126(1)$, $b = 11.216(2)$, $c = 9.680(1)$ Å, $\beta = 98.57(1)°$, $U = 765.0(2)$ Å^3, $Z = 4$, $D_c = 1.820$ g cm^{-3}, space group $P2_1/c$], so that the formula given in that reference is incorrect.

Disodium glyphosate nonahydrate **6** represents a structural contrast to the other sodium glyphosate polymorphs reported here. Whereas with **3** and **5** the polymeric structures involve the glyphosate ligands intimately in bridging modes, the structure of **6** has discrete $[Na(HL)(H_2O)_5]^-$ anion units together with $[Na_2(H_2O)_8]_n^{2n+}$ ribbon polymeric cationic chains (Fig. 5) linked by extensive hydrogen bonding. The structure is therefore best represented as $[Na_2(H_2O)_8][Na(HL)(H_2O)_5]_{2n}$ with the average nonahydrate formula. The regular octahedral six-co-ordinate monomeric anion units involve five unidentate water ligands [O(10)–O(14): Na(1)–O, 2.353–2.523(3) Å] and a single carboxylate oxygen from the glyphosate ligand [Na(1)–O(1), 2.429(3) Å]. This unidentate co-ordination mode represents the first example of its type with any metal species with glyphosate and is in this circumstance unexpected considering the ambivalent nature of the ligand and the precedent set by the previous two examples. The ribbon polymer comprising the cationic part of this structure is best described as a repeating bis-aqua bridged dimer. Each octahedral Na(2) centre in the dimer is linked by the water molecules O(7) and O(8) and is related by crystallographic 2_1 screw symmetry while the six-co-ordination is completed by two non-bridging water ligands [O(6), O(9)], the Na–O range and mean being 2.394–2.536(3) and 2.433 Å, respectively. This structure is very similar to those of Glauber's salt $Na_2SO_4\cdot 10H_2O$[19,20] and borax $Na_2B_4O_7\cdot 10H_2O$.[20] The only differences lie in the symmetry relating the units in the ribbon [glide plane in Glauber's salt and inversion in borax]. In both of these structures the polymer cation chains are linked to the anions by extensive hydrogen bonding, in Glauber's salt, *via* two intermediate lattice water molecules {essentially $[Na_2(H_2O)_8]_n$ $[SO_4]_n\cdot 2nH_2O$} and in borax directly to the cyclic tetraborate ions {$[Na_2(H_2O)_8]_n$ $[(B_4O_5)(OH)_4]_n$}. Both of these systems are analogous to the hydrogen-bonded network found in the structure of **6**, where a total of 13 strong internal hydrogen bonds are identified (Fig. 6 and Table 2), involving phosphonate oxygens [O(3), O(4) and O(5) (three each)], the non-bonded carboxylate oxygen [O(2) (three)] and the protonated imine nitrogen N(1) (one: with both bridging and non-bridging cation chain waters, as well as with the co-ordinated waters on the anionic complex).

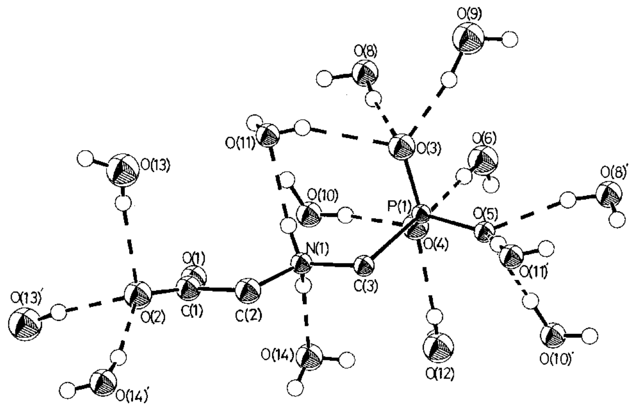
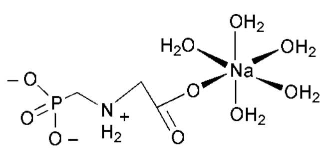
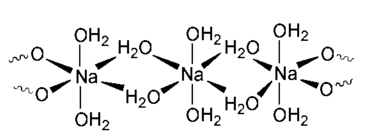


Fig. 6 Hydrogen bonding interactions involving the glyphosate ligand in compound **6**.



$[Na(HL)(H_2O)_5]^-$



$[\{Na_2(H_2O)_8]^{2+}\}_n$

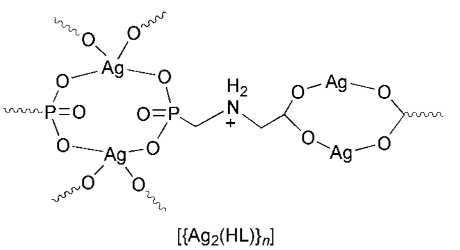
Compound **6** is assumed to be identical to that reported in ref. 2, having the same formula. However, the crystal data reported [$a = 6.732(1)$, $b = 7.185(1)$, $c = 17.808(3)$ Å,

Table 1 Bond distances (Å) and angles (°) about the co-ordination polyhedra in compounds **3**, **4** and **6**

Compound **3**					
Na(1)–O(1)^{a}	2.344(2)	Na(1)–O(3)^{a}	2.432(2)	Na(2)–O(6)	2.381(2)
Na(1)–O(6)	2.349(2)	Na(1)–O(2′)^{b}	2.583(2)	Na(2)–O(2′)^{b}	2.409(2)
Na(1)–O(4)	2.361(2)	Na(2)–O(4′)^{c}	2.358(2)	Na(2)–O(5′)^{b}	2.497(2)
Na(1)–O(5)^{b}	2.401(2)	Na(2)–O(3′)^{d}	2.359(2)	Na(2)–O(1)^{a}	2.534(2)
O(1)^{a}–Na(1)–O(6)	81.46(6)	O(4)–Na(1)–O(3)^{a}	87.71(5)	O(3′)^{d}–Na(2)–O(6)	107.04(6)
O(1)^{a}–Na(1)–O(4)	86.88(5)	O(4)–Na(1)–O(2′)^{b}	104.80(5)	O(3′)^{d}–Na(2)–O(2′)^{b}	84.58(5)
O(1)^{a}–Na(1)–O(5)^{b}	160.42(6)	O(5)^{b}–Na(1)–O(3)^{a}	103.10(5)	O(3′)^{d}–Na(2)–O(5′)^{b}	92.00(5)
O(1)^{a}–Na(1)–O(3)^{a}	96.48(5)	O(5)^{b}–Na(1)–O(2′)^{b}	78.80(5)	O(3′)^{d}–Na(2)–O(1)^{a}	165.10(6)
O(1)^{a}–Na(1)–O(2′)^{b}	82.05(5)	O(3)^{a}–Na(1)–O(2′)^{b}	167.26(5)	O(6)–Na(2)–O(2′)^{b}	81.45(5)
O(6)–Na(1)–O(4)	161.37(6)	O(4′)^{c}–Na(2)–O(3′)^{d}	91.25(5)	O(6)–Na(2)–O(5′)^{b}	158.37(6)
O(6)–Na(1)–O(5)^{b}	98.52(6)	O(4′)^{c}–Na(2)–O(6)	108.39(6)	O(6)–Na(2)–O(1)^{a}	77.01(5)
O(6)–Na(1)–O(3)^{a}	88.79(5)	O(4′)^{c}–Na(2)–O(2′)^{b}	170.10(5)	O(2′)^{b}–Na(2)–O(5′)^{b}	90.47(5)
O(6)–Na(1)–O(2′)^{b}	78.47(5)	O(4′)^{c}–Na(2)–O(5′)^{b}	80.68(5)	O(2′)^{b}–Na(2)–O(1)^{a}	81.84(5)
O(4)–Na(1)–O(5)^{b}	94.09(5)	O(4′)–Na(2)–O(1)^{a}	101.16(5)	O(5′)^{b}–Na(2)–O(1)^{a}	82.02(5)
Symmetry relations: a $1 - x, \frac{1}{2} - y, \frac{1}{2} + z$; b $1 - x, -y, 1 - z$; c $1 - x, \frac{1}{2} + y, 1\frac{1}{2} - z$; d $-1 + x, y, z$.					
Compound **4**					
Na–O(4)^{a}	2.367(1)	Na–O(1)^{b}	2.378(1)	Na–O(2)	2.474(1)
Na–O(5)^{b}	2.374(1)	Na–O(5)^{c}	2.389(1)	Na–O(6)	2.586(2)
O(4)^{a}–Na–O(5)^{b}	89.19(4)	O(5)^{b}–Na–O(1)^{b}	90.12(4)	O(1)^{b}–Na–O(2)	101.63(5)
O(4)^{a}–Na–O(1)^{b}	84.99(4)	O(5)^{b}–Na–O(5)^{c}	89.29(4)	O(1)^{b}–Na–O(6)	164.13(5)
O(4)^{a}–Na–O(5)^{c}	173.46(5)	O(5)^{b}–Na–O(2)	168.17(5)	O(5)^{c}–Na–O(2)	89.63(4)
O(4)^{a}–Na–O(2)	93.14(4)	O(5)^{b}–Na–O(6)	74.05(5)	O(5)^{c}–Na–O(6)	90.09(4)
O(4)^{a}–Na–O(6)	95.61(4)	O(1)^{b}–Na–O(5)^{c}	88.66(4)	O(2)–Na–O(6)	94.17(5)
Symmetry relations: a $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; b $x, 1\frac{1}{2} - y, -\frac{1}{2} + z$; c $-x, \frac{1}{2} + y, \frac{1}{2} - z$.					
Compound **6**					
Na(1)–O(13)	2.353(3)	Na(1)–O(10)	2.440(2)	Na(2)–O(8)^{a}	2.394(2)
Na(1)–O(14)	2.406(2)	Na(1)–O(12)	2.523(3)	Na(2)–O(9)	2.447(3)
Na(1)–O(11)	2.413(2)	Na(2)–O(6)	2.383(3)	Na(2)–O(7)	2.445(3)
Na(1)–O(1)	2.429(3)	Na(2)–O(8)	2.395(2)	Na(2)–O(7)	2.536(3)
O(13)–Na(1)–O(14)	104.8(1)	O(11)–Na(1)–O(10)	89.7(1)	O(8)–Na(2)–O(8)^{a}	176.9(1)
O(13)–Na(1)–O(11)	92.5(1)	O(11)–Na(1)–O(12)	85.4(1)	O(8)–Na(2)–O(9)	87.2(1)
O(13)–Na(1)–O(1)	92.7(1)	O(1)–Na(1)–O(10)	87.6(1)	O(8)–Na(2)–O(7)	96.3(1)
O(13)–Na(1)–O(10)	170.9(1)	O(1)–Na(1)–O(12)	109.4(1)	O(8)–Na(2)–O(7)	81.1(1)
O(13)–Na(1)–O(12)	92.1(1)	O(10)–Na(1)–O(12)	79.3(1)	O(8)^{a}–Na(2)–O(9)	95.9(1)
O(14)–Na(1)–O(11)	85.7(1)	O(6)–Na(2)–O(8)	87.8(1)	O(8)^{a}–Na(2)–O(7)	83.0(1)
O(14)–Na(1)–O(1)	78.5(1)	O(6)–Na(2)–O(8)^{a}	89.1(1)	O(8)^{a}–Na(2)–O(7)	99.5(1)
O(14)–Na(1)–O(10)	84.2(1)	O(6)–Na(2)–O(9)	173.2(1)	O(9)–Na(2)–O(7)	95.8(1)
O(14)–Na(1)–O(12)	161.2(1)	O(6)–Na(2)–O(7)	89.3(1)	O(9)–Na(2)–O(7)	87.8(1)
O(11)–Na(1)–O(1)	164.1(1)	O(6)–Na(2)–O(7)	86.9(1)	O(7)–Na(2)–O(7)	175.5(1)
Symmetry relations: a $-x, -\frac{1}{2} + y, -z$; b $1 - x, \frac{1}{2} + y, -z$.					

$\beta = 94.06(1)°$, $U = 813.2(2)$ Å^3, $Z = 2$, $D_c = 1.45$g cm^{-3}, space group $P2_1$] are inconsistent and in obvious error.

The structure of complex **7**, $[Ag_2(HL)]_n$, although not satisfactorily refined because of a previously mentioned twinning problem, is considered of sufficient precision to allow a meaningful description of the molecular configuration. The mode of complexation is consistent with the known chemistry particularly of silver(I) carboxylates[21,22] and supported by infrared spectroscopy. All oxygens of the phosphonate group are co-ordinated to two silver atoms, one at a general position [four-co-ordinate tetrahedral] and the other at an inversion centre [two-co-ordinate linear]. A number of relatively short Ag···Ag contacts (four) are present (3.08–3.27 Å) while the Ag–O distance range and mean are 2.21–2.53 and 2.33 Å, respectively. The carboxylate group, which is considerably disordered, is associated with another silver in a characteristic centrosymmetric bis(carboxylato-*O*,*O′*) co-ordination mode [Ag···Ag, 2.86: Ag–O, 2.31, 2.43 Å]. The Ag···Ag separation is considered average within range found for similar Type 1 silver carboxylate dimers (2.78– 2.97 Å[22]). The resulting alternating head to head and tail to tail glyphosate ligands and their co-ordinated metal centres form a continuous polymer chain with few inter-chain associations, resulting in the hard, dense crystal morphology.



[{Ag$_2$(HL)}$_n$]

Infrared spectroscopy

The infrared spectrum of glyphosate[23] shows characteristic bands for both the free CO_2H stretching (1732 cm^{-1}) and hydrogen-bonded CO_2H stretching (1717 and 1422 cm^{-1}), together with those for the phosphonate group and the protonated amine group. Table 3 lists these bands and the comparative values for the complexes reported in this work. All complexes exhibit comparative frequencies which reflect the varying degrees of co-ordination. The ammonium salt $[NH_4][H_2L]$ **1** shows a simple carboxylate structure with asymmetric and symmetric CO_2^- frequencies at 1631 and 1402 cm^{-1} respectively. Consistent with structural findings, all of the sodium analogues show vibrational frequencies typical of metal bonded carboxylates, with the $\Delta(\nu_{asym} - \nu_{sym})$ values ranging from the more typical value of 221 (**3**) to 235 cm^{-1} (**4**). This larger value for **4** may or may not be significant.[24] The CO_2^- region of the spectrum of the dihydrate **5** is quite anomalous compared to **3** and **4** with a broad band centred at 1614 cm^{-1} and a shoulder at 1660 cm^{-1}, possibly resulting from an unresolved combination of the asymmetric CO_2^- and NH_2^+ vibrations. For the lithium analogue **2** the CO_2^- (ν_{asym}) (1673 cm^{-1}) and NH_2^+ (δ) (1628 and 1599 cm^{-1}) vibrations, as expected, are slightly different from those for the sodium series. The two NH_2^+ vibrations indicate that the glyphosate ligand exists in two different environments and may also indicate a carboxylate group bridging Li. The spectra of the nonahydrate **6**, the silver complex **7** and the potassium analogue K_3L[23] all show similar characteristics with relatively broad bands for CO_2^- (ν_{asym}) (1631, 1588 and 1631 cm^{-1}) and (ν_{sym}) (1408, 1403 and 1399 cm^{-1}) respectively. The lowered frequencies for the silver complex **7** compared to those of the sodium analogues are to be expected with the greater co-ordinating strength of Ag *cf.* Na.

Table 2 Hydrogen bond contacts

Contact D···A	Bond length *d*/Å	Bond angle D–H···A/°
Compound **1**		
N(1)···O(1)	2.82	158
N(1)···O(3)	2.72	168
O(1)···O(3)	2.53	166
N(2)···O(1)	2.78	164
N(2)···O(2)	3.01	164
N(2)···O(3)	2.89	159
N(2)···O(5)	2.92	166
Compound **3**		
N(1)···O(3)	2.73	173
N(1)···O(4)	2.71	163
O(5)···O(1′)	2.56	176
O(6)···O(1′)	2.80	163
O(6)···O(2)	2.75	168
N(1′)···O(3′)	2.79	161
N(1′)···O(4′)	2.70	166
O(5′)···O(2)	2.58	176
Compound **4**		
N(1)···O(4)	2.75	167
O(3)···O(2)	2.62	168
O(3)···O(1)	3.18	130
O(6)···O(1)	2.90	165
O(6)···O(2)	2.94	162
Compound **6**		
N(1)···O(11)	2.82	151
N(1)···O(14)	2.86	160
O(6)···O(4)	2.71	168
O(6)···O(9)	2.73	176
O(7)···O(10)	2.78	158
O(8)···O(3)	2.97	169
O(8)···O(5)	2.75	167
O(9)···O(3)	2.70	162
O(9)···O(6)	2.75	173
O(10)···O(4)	2.77	161
O(10)···O(5)	2.80	175
O(11)···O(3)	2.86	155
O(11)···O(5)	2.70	168
O(12)···O(3)	2.91	148
O(12)···O(4)	2.77	175
O(13)···O(2)	2.74	171
O(13)···O(2′)	2.90	172
O(14)···O(2)	2.72	170
O(14)···O(12)	2.79	166

The NH_2^+ deformations of compound **1** at 1567 and 1488 cm^{-1} compare well with 1557 and 1483 cm^{-1} for glyphosate, indicating very similar environments. As in the spectrum for **2**, these vibrations for the hemi-hydrate **3** show a doublet at 1601 and 1580 cm^{-1}, indicative of the two different environments found for the glyphosate ligand in the crystal structure, while the monohydrate **4** shows only one frequency, consistent with the observed single ligand environment. The equivalent vibrations in the structures of the dihydrate **5**, the nonahydrate **6** and the silver complex **7** could not be assigned.

The phosphate group in glyphosate hydrochloride and in glyphosine [$HO_2CCH_2N(CH_2PO_3H_2)$] gives an absorption at 1309 cm^{-1} attributed to the non-hydrogen bonded P=O group.[23] In glyphosate, which reverts to the zwitterion form, the P···O bond loses some of its double-bond character and absorbs at 1268 cm^{-1}. All members of the series are similar (range 1265–1279 cm^{-1}) except the hemi-hydrate **3** (1302 cm^{-1}) which suggests that in the latter the P=O character is maximized. It appears that the delocalization of the PO_3 group due to hydrogen bonding or to bonding to sodium is roughly the same in all compounds.

The PO_3H^- or P–O$^-$ symmetric vibrations for all members of this series occur over a narrow range (1106–1084 cm^{-1}). The similarity extends to P–O–H vibrations except that in the monohydrate **4**, where the group is free, the frequency is shifted to higher energy. The frequencies for the ammonium salt would thus indicate strong hydrogen bonding to the P–O–H group, while in the dihydrate **5** it can be assumed that the P–O–H group is bonded to Na.

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Table 3 Characteristic glyphosate vibrational bands (cm^{-1})

	$H_3L^{a,b}$	1	2	3	4	5	6	7	K_3L^{b}
CO_2^- (asym)	1732 (nhb) 1717 (hb)	1631	1673	1621	1624	1614	1631	1588	1631
(sym)	1422	1402	1425	1400	1389	1388	1408	1403	1399
$\Delta(\nu_{asym} - \nu_{sym})$	—	229	248	221	235	226	223	185	232
NH_2^+ (def.)	1557	1567	1628 1599	1601 1580	1592	?	?	?	—
NH_2^+ (def.)	1483	1488	1504	1505	1505	?	?	?	—
P=O (asym)	1268	1271	1268	1302	1265	1279 (weak)	—	1274	—
P–O$^-$ (sym)	1090	1106	1096	1084	1090	1084	—	1087	—
P–O–H (asym)	1166	1167	unresolved	1164	1187	1160	—	1187	—
PO_3^{2-} (asym)	—	—	—	—	—	—	unresolved	—	1172
PO_3^{2-} (sym)	—	—	—	—	—	—	1089	—	1083

nhb = non-hydrogen bonded, hb = hydrogen bonded. [a] Ref. 24. [b] Ref. 23.

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