Tabelle 2. *Ausgewählte interatomare Abstände* (Å) *mit Standardabweichungen in Klammern*

Ba(1)–O($3^{i,iv}$)	2,809 (7)	–O(1)	2,825 (10)
–O($2^{ii,iii}$)	2,8486 (8)	–O($3^{v,vii}$)	2,917 (7)
–O(2^{viii})	3,034 (10)	–O($5^{iii,vi}$)	3,098 (7)
–O($4^{v,vii}$)	3,346 (7)		
Ba(2)–O(2)	2,621 (10)	–O($3^{i,iv}$)	2,827 (7)
–O($1^{i,iv}$)	2,8394 (2)	–O($5^{iii,vi}$)	2,904 (7)
–O(5^{xi})	3,151 (7)	–O($4^{ix,xiii}$)	3,192 (7)
–O(5)	3,151 (7)		
Cu –O($4^{i,iv}$)	1,981 (7)	–O($3^{i,iv}$)	2,013 (7)
–O(2^{viii})	2,112 (10)		
Pt –O(2^{x})	2,007 (10)	–O($5^{x,xii}$)	2,030 (7)
–O(3^{xi})	2,038 (7)	–O(1)	2,084 (10)
–O(3)	2,038 (7)		
Y(1) –O($4^{v,vii}$)	2,265 (7)	–O($4^{iii,vi}$)	2,313 (7)
–O($5^{x,xii}$)	2,366 (7)	–O(1)	2,370 (10)
Y(2) –O($5^{iii,vi}$)	2,227 (7)	–O(3^{xi})	2,312 (7)
–O(4^{xi})	2,354 (7)	–O(1)	2,423 (10)
–O(3)	2,312 (7)	–O(4)	2,354 (7)

Symmetrieoperationen: (i) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (ii) $\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$; (iii) $\frac{1}{2}-x, -y, -\frac{1}{2}+z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (v) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}+z$; (vii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; (viii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{2}-z$; (ix) $-x, -y, 1-z$; (x) $x, y, -1+z$; (xi) $x, \frac{1}{2}-y, z$; (xii) $x, \frac{1}{2}-y, -1+z$; (xiii) $-x, \frac{1}{2}+y, 1-z$.

$CdPt_3O_6$ ist das vierwertige Pt-Atom oktaedrisch von sechs O-Atomen umgeben, während das zweiwertige Pt-Atom eine quadratisch planare [4]-Koordination annimmt (Prewitt, Schwartz & Shannon, 1983). Somit ist das [6]-koordinierte Pt-Atom im $Ba_2CuPtY_2O_8$ wahrscheinlich vierwertig. Da alle O-Lagen zweifelsfrei vollständig besetzt sind, muß das Cu-Atom zweiwertig sein. Die interatomaren Abstände sind in Tabelle 2 zusammengestellt; die Mittelwerte für einzelne Metallatome stimmen mit den von den Ionenradien (Shannon, 1976) erwarteten werten überein.

Die untersuchten Einkristalle des $Ba_2CuPtY_2O_8$ wiesen bei Raumtemperatur keine nennenswerte elektrische Leitfähigkeit auf.

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Preparation and X-ray Structure of the Calcium(II) Complex of *N*-Phosphonomethylglycine $Ca[O_2CCH_2NH_2CH_2PO_3].2H_2O$ at pH 7·2

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Abstract. $M_r = 243\cdot17$, triclinic, $P\bar{1}$, $a = 7\cdot9497$ (4), $b = 10\cdot3985$ (4), $c = 5\cdot4287$ (4) Å, $\alpha = 101\cdot544$ (4), $\beta = 96\cdot950$ (5), $\gamma = 74\cdot506$ (4)°, $V = 422\cdot61$ (4) Å^3, $Z = 2$, $D_x = 1\cdot91$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1\cdot54178$ Å, $\mu = 81\cdot34$ cm^{-1}, $F(000) = 252$, $T = 295$ K, $R = 0\cdot029$ for 1094 unique observed reflections. The Ca^{2+} ion is seven-coordinate with two *cis*-water ligands and two coordinate bonds to O2 and O3 of the phosphonate group of *N*-phosphonomethylglycine (pmg). The remaining coordination involves O1 and O3 of symmetry-related phosphonate groups and O9 from a symmetry-related carboxylic acid group. The coordination at pH 7·2 may be described as an infinite array of unfolded *N*-protonated pmg ligands that coordinate to Ca^{II} to form four-membered chelate rings.

Introduction. *N*-Phosphonomethylglycine (pmg), first described by Toy & Whing (1964), is a member of the

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chelating group of amino-polyacid series which includes both aminocarboxylic acid and alkylphosphonic acid functions. The coordination chemistry of pmg in solution has been compared to that of the common chelates that contain carboxylate and phosphonate ligand groups (Motekaitis & Martell, 1985). The behavior of pmg as a potent herbicide that is readily translocated in plant tissue and deactivated in soil (Sprankle, Meggitt & Penner, 1975) may be explained partly by its chelate chemistry.

The tendency of divalent alkaline-earth and transition metals to form 1:1 and 2:1 metal complexes with pmg has been determined by potentiometric equilibrium measurements (Motekaitis & Martell, 1985), extending and supplementing earlier reports (Madsen, Christensen & Gottlieb-Petersen, 1978). Highly basic divalent metal ions such as those of Ca^{II} and Mg^{II} tend to form weak 1:1 metal chelates with pmg, whereas divalent and trivalent transition-metal ions such as Ni^{II} and Cu^{II} are more strongly chelated. Most metal ions also form 2:1 metal complexes with pmg at high pH, but the degree of formation of 2:1 complexes is limited by the stability and/or insolubility of the hydroxides and hydroxo complexes of the metal ions which predominate under extremely alkaline conditions (Motekaitis & Martell, 1985).

The tendency of pmg to form metal chelates may also be considered in terms of the basicity of the donor groups. Motekaitis & Martell (1985) reported that the protonation constants of pmg are 10·14, 5·46 and 2·23. These were assigned to the amino N, the pair of equivalent phosphonate O atoms, and the carboxylate O atoms, respectively. Furthermore, they found that at pH 7, metal ions initially form weak complexes with the protonated MHL species, and the stabilities of the metal chelates increase as the proton is dissociated from the complex at higher pH. The low stabilities of the MHL-type complexes and the high dissociation constant of the protonated MHL species suggest that the site of the proton in pmg is the amino N. Protonation of the amino N atom would be expected to prevent the formation of chelate rings involving simultaneous coordination of the metal ion by phosphonate O, carboxylate O and amino N donors.

The order of the observed protonation constants for pmg suggests that the neutral acid exists in the zwitterionic form as $NH_2^+(CH_2COOH)(CH_2PO_3H^-)$. This betaine form was confirmed by the X-ray crystal structure of the free acid (Sheldrick & Morr, 1981), and also by assignment of ^{31}P NMR shifts for the solution complex of platinum(II)–*N*-phosphonomethylglycine (Appleton, Hall & McMahon, 1986). Shkol'nikova, Porai-Koshits, Dyatlova, Yaroshenko, Rudomino & Kolova (1983) provided structural proof on the basis of single-crystal X-ray studies that the protons participating in intramolecular H-bonded frameworks of the acid form of pmg are supplied by the phosphonic and not the carboxylic acid groups. X-ray diffraction crystal structures of the free pmg show that a proton resides on the amino N (Sheldrick & Morr, 1981).

It was the purpose of the present study to prepare a series of metal complexes with pmg and to characterize these complexes by single-crystal X-ray diffraction techniques. In this first paper we report the preparation of the hydrated calcium pmg complex at physiological pH and its structural elucidation by single-crystal X-ray methods.

Experimental. *N*-Phosphonomethylglycine (5·0 g, 30 mmol, Stauffer), 99·34% purity by titration (Motekaitis & Martell, 1985), and $Ca(NO_3)_2.4H_2O$ (7·1 g, 30 mmol, Fisher certified), dissolved in a minimum of hot water. Solution adjusted to pH = 7·2 by addition of NaOH. Filtered immediately to remove yellow pmg impurity. Eluant cooled, crystallization by slow evaporation/controlled dilution over 12 weeks. Analysis: C 14·63 (14·81); N 5·61 (5·76); H 4·02 (4·11)%.

X-ray analysis using a colorless parallelepiped crystal, 0·08 × 0·04 × 0·12 mm, glass fiber, random orientation, cell parameters from 25 high-angle reflections ($2\theta > 108°$), Rigaku AFC-5R diffractometer (rotating anode), incident-beam graphite monochromator, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54178$ Å, *CONTROL* program set in AUTO mode (Molecular Structure Corporation, 1986*a*). Scans by θ–2θ method; 32° (θ) min^{-1}; maximum of three scans for weak data, background 50% of scan time. Scan width $\Delta\omega = A + B \tan\theta$. Here B was 0·300° and A was experimentally determined to be 0·155° (ω); standards ($\bar{3}\bar{3}1$, $2\bar{3}0$, $1\bar{4}1$) automatically chosen based on intensity and spatial distribution, measured every 150 measurements, no drop in intensity; no crystal reorientation necessary. Absorption correction by ψ-scan method (Coppens, Leiserowitz & Rabinovich, 1965); transmission 0·702–1·0, average = 0·869; ψ-scan reflections chosen automatically.

Intensity as $C - \frac{1}{2}(t_c/t_b)(b_1 + b_2)$ where C = total number of counts, t_c = time spent counting peak intensity, t_b = time spent counting one side of background, b_1 = high-angle background counts, b_2 = low-angle background counts; the intensity error $\sigma(F^2) = [C + \frac{1}{4}(t_c/t_b)^2(b_1 + b_2) + (pI)^2]^{1/2}$ where I is the intensity and the p factor took the value of 0·05. Lorentz and polarization corrections applied; weights as $1/\sigma^2(F_o)$. Neutral-atom scattering factors (Cromer & Waber, 1974; Stewart, Davidson & Simpson, 1965). Anomalous dispersion from Cromer (1974).

A total of 1226 reflections collected with $0 < 2\theta < 120°$ ($h = 0$ to 9, $k = -12$ to 12, $l = -6$ to 6), 81 averaged ($R_{av} = 0{\cdot}5\%$), 1094 $I > 3\sigma(I)$. Direct methods, *MITHRIL* (Gilmore, 1983) for Ca and P atoms, remaining structure by full-matrix least-squares refinement of F with positional and anisotropic temperature factors. H atoms located by difference Fourier synthesis, refined positionally and isotropically. Final residuals $R = 0{\cdot}029$, $wR = 0{\cdot}045$, $S = 1{\cdot}52$; maximum shift $\Delta/\sigma < 3$ (hydrogen β value); largest peak in difference Fourier map $<0{\cdot}2$ e Å^{-3}. VAX 11/780 using *TEXSAN* program package (Molecular Structure Corporation, 1986*b*).

Discussion. Positional and equivalent isotropic thermal parameters are given in Table 1.* Fig. 1 gives the Ca coordination, pmg numbering scheme and important bond distances in the complex. Fig. 2 highlights the arrangement relative to the unit cell showing the three-dimensionality of the structure. Important bond angles and torsional angles are given in Table 2. Two Ca.pmg.2H_2O units occur in the unit cell with Ca being seven-coordinate. This coordination comprises the two water molecules O20 and O21 *cis* to each other; *trans* to O20 is O1 from a symmetry-related phosphonate group and *trans* to O21 is the non-bonded P of the phosphonate group [176·11 (7)°] which makes its coordination through phosphonate oxygens O2 and O3.

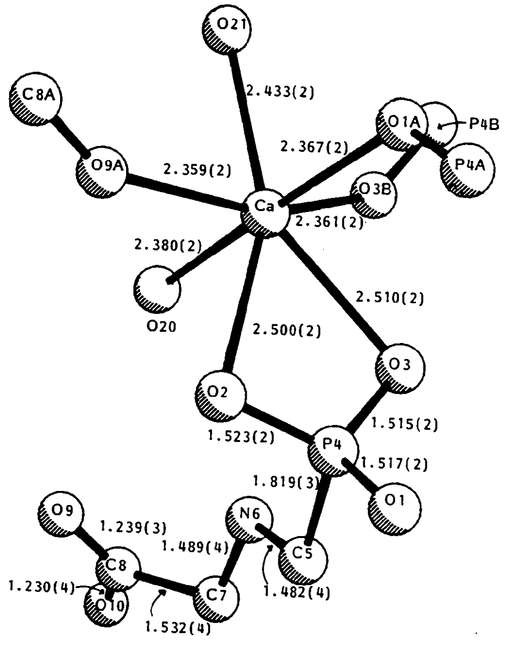

Fig. 1. Calcium(II)–pmg dihydrate showing the seven-coordination of Ca, the numbering scheme and the intra- and intermolecular distances (Å). H atoms have been omitted for clarity. Atoms designated *A* and *B* come from symmetry-related pmg ligands.

Table 1. *Positional parameters and equivalent isotropic thermal parameters*

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
Ca	0·29584 (6)	0·12630 (5)	0·1599 (1)	1·06 (3)
P4	0·41300 (8)	−0·15766 (6)	0·3011 (1)	1·03 (3)
O1	0·5019 (2)	−0·2108 (2)	0·5370 (4)	1·46 (8)
O2	0·2344 (2)	−0·0589 (2)	0·3382 (4)	1·59 (8)
O3	0·5198 (2)	−0·0950 (2)	0·1685 (3)	1·40 (8)
O9	−0·0406 (2)	−0·2329 (2)	−0·3752 (4)	2·3 (1)
O10	0·0328 (3)	−0·4070 (2)	−0·6865 (4)	2·9 (1)
O20	0·1186 (3)	0·0397 (2)	−0·1851 (4)	2·1 (1)
O21	0·2235 (3)	0·3524 (2)	0·0546 (5)	2·2 (1)
N6	0·2868 (3)	−0·2724 (2)	−0·1597 (5)	1·6 (1)
C5	0·3752 (4)	−0·3065 (3)	0·0837 (6)	1·6 (1)
C7	0·2344 (4)	−0·3867 (3)	−0·3363 (6)	1·8 (1)
C8	0·0590 (4)	−0·3370 (3)	−0·4816 (6)	1·6 (1)
H51	0·304 (4)	−0·348 (3)	0·155 (6)	1·8 (6)
H52	0·475 (5)	−0·376 (4)	0·043 (7)	3·0 (7)
H61	0·359 (4)	−0·235 (3)	−0·250 (6)	2·7 (7)
H62	0·195 (5)	−0·207 (4)	−0·138 (7)	3·4 (8)
H71	0·336 (4)	−0·442 (3)	−0·451 (7)	2·4 (7)
H72	0·218 (4)	−0·449 (3)	−0·223 (6)	2·9 (7)
H200	0·151 (5)	0·031 (4)	−0·327 (8)	3 (1)
H201	0·013 (6)	0·027 (5)	−0·224 (8)	5 (1)
H210	0·179 (5)	0·419 (4)	0·158 (8)	3·5 (9)
H211	0·142 (5)	0·353 (4)	−0·095 (8)	3·5 (8)

Table 2. *Bond angles (°) and torsional angles (°) with e.s.d.'s in parentheses*

O9—Ca—O3′	153·38 (8)	O1—Ca—O3	82·90 (6)
O9—Ca—O1	97·81 (7)	O20—Ca—O21	94·27 (9)
O9—Ca—O20	88·89 (8)	O20—Ca—O2	80·73 (8)
O9—Ca—O21	78·15 (8)	O20—Ca—O3	95·10 (7)
O9—Ca—O2	75·98 (7)	O21—Ca—O2	153·71 (7)
O9—Ca—O3	133·11 (7)	O21—Ca—O3	147·43 (7)
O3′—Ca—O1	91·88 (7)	O21—Ca—P4	176·11 (7)
O3′—Ca—O20	80·57 (8)	O2—Ca—O3	58·81 (6)
O3′—Ca—O21	78·35 (7)	O3—P4—O1	115·8 (1)
O3′—Ca—O2	125·50 (6)	O3—P4—O2	108·1 (1)
O3′—Ca—O3	72·56 (7)	O3—P4—C5	106·7 (1)
O1—Ca—O20	172·44 (8)	O1—P4—O2	114·2 (1)
O1—Ca—O21	83·75 (8)	O1—P4—C5	104·8 (1)
O1—Ca—O2	104·23 (7)	O2—P4—C5	106·5 (1)
O3—P4—C5—N6	−57·1 (2)	P4—C5—N6—C7	−173·7 (2)
O9—C8—C7—N6	−26·6 (4)	O1—P4—C5—N6	179·6 (2)
O10—C8—C7—N6	155·1 (3)	O2—P4—C5—N6	58·2 (2)
C5—N6—C7—C8	143·1 (3)		

The remaining coordination comes from C9 of a symmetry-related carboxylic acid group and an O3 from a symmetry-related phosphonate group. Thus each Ca is coordinated by four different pmg molecules. The role of the non-bonded P is that of expansion of the coordination sphere by introduction of the four-membered chelate comprising Ca—O2—P4—O3. The Ca—P distance in this chelate is 3·072(1)Å. P retains a nearly perfect T_d geometry. The phosphonate oxygen O3, it is interesting to note, acts as a bridge between two Ca ions. The N atom of pmg is diprotonated with near tetrahedral hydrogens and charge compensation in the ligand is accomplished by loss of the carboxylic acid H atom.

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44662 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure is therefore polymeric with linking in all three directions. The atoms O1*A* and O3*B* are from pmg's separated in **c** by one unit cell. The bonding of pmg is such as to leave O10 free in space. This atom has its coordination satisfied by one symmetric hydrogen bond in the **c** direction with water hydrogen H211 [1·76 (4) Å] and one asymmetric hydrogen bond in the **bc** direction with water hydrogen [1·96 (4) Å]. It is this linking that holds the structure together in the **b** direction. The remaining bonding scheme consists of O1—H61 in the **c** direction, 1·81 (4) Å, and O2—H200 along **c**, 1·97 (4) Å. The crystal structure thus shows ligand and H-bonding along **c**, ligand bonding along **a** and only H-bonding along the **b** direction. Torsional angles of importance, listed in Table 2, show that O1—P4—C5—N6 is a nearly perfect *trans*-arrangement [179·6 (2)°], as is P4—C5—N6—C7 [−173·7 (2)°].

The results of this single-crystal study are interesting in two main aspects. Firstly, pmg although chelated is not chelated in a wrap-around fashion but through the formation of a four-membered chelate ring associated with the phosphonate group only. Secondly, the N is protonated and the carboxylic acid is deprotonated at physiological pH. This is in agreement with the potentiometric work of Motekaitis & Martell (1985). There is similarity to the free pmg ligand which has a protonated amine N, but charge balance is achieved by having the carboxylic and phosphonate functional groups protonated as well (Shkol'nikova, Porai-Koshits, Dyatlova, Yaroshenko, Rudomino & Kolova, 1983). The configuration of the free ligand, however, seems to be somewhat more elongated than that of the Ca^{II} complex in this study. The conformation is basically the same, although torsional angles indicate that the phosphonate group is twisted *ca* 20° from the free ligand structure (O3—P4—C5—N6 −57·1 *versus* −37·7° in the free ligand), C5—N6—C7—C8 is twisted by *ca* 30° and the carboxylic group by *ca* 25° (N6—C7—C8—O9 1·5 *versus* −27·0°). Apparently, the requirements of the chelate ring and bonding of O9 of the acid group cause this slight change in conformation. The positively charged N group and negatively charged carboxylic acid functional groups seen in this study prove that in the physiological pH range the zwitterionic structure of the chelate is present. This is consistent with results found with other chelating agents of the aminocarboxylic acid series that have been previously studied (Shkol'nikova, Porai-Koshits & Dyatlova, 1986). The second general feature of hydrogen-bonding rings is also seen with the N6—H6—O1PO_2 ring system. This is a relatively strong bond for such systems with O1—H61 at 1·81 (4) Å and the N6—H61—O1 angle close to 165°, although H61 is not bifurcate. In all previously studied systems a bifurcate H was seen.

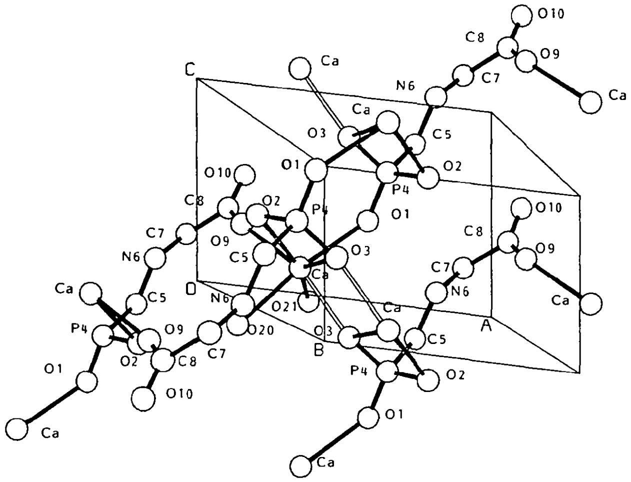

Fig. 2. The relationship of pmg packing in the unit cell. The orientation shows one fully coordinated Ca and the unfolded nature of pmg. The non-chelating O3 contact to Ca has been left unshaded for clarity.

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