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Poly[aqua[μ_3-(pyridin-1-ium-3,5-diyl)diphosphonato-κ^3O:O':O''][μ_2-(pyridin-1-ium-3,5-diyl)diphosphonato-κ^2O:O']calcium(II)]

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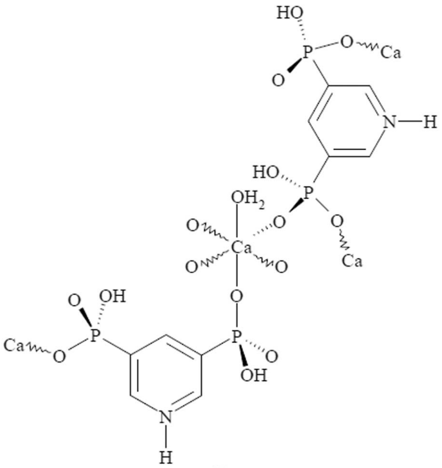
The rigid organic ligand (pyridine-3,5-diyl)diphosphonic acid has been used to create the title novel three-dimensional coordination polymer, $[Ca(C_5H_6NO_6P_2)_2(H_2O)]_n$. The six-coordinate calcium ion is in a distorted octahedral environment, formed by five phosphonate O atoms from five different (pyridin-1-ium-3,5-diyl)diphosphonate ligands, two of which are unique, and one water O atom. Two crystallographically independent acid monoanions, *L*1 and *L*2, serve to link metal centres using two different coordination modes, *viz.* $\eta^2\mu_2$ and $\eta^3\mu_3$, respectively. The latter ligand, *L*2, forms a strongly undulated two-dimensional framework parallel to the crystallographic *bc* plane, whereas the former ligand, *L*1, is utilized in the formation of one-dimensional helical chains in the [010] direction. The two sublattices of *L*1 and *L*2 interweave at the Ca^{2+} ions to form a three-dimensional framework. In addition, multiple O—H···O and N—H···O hydrogen bonds stabilize the three-dimensional coordination network. Topologically, the three-dimensional framework can be simplified as a very unusual (2,3,5)-connected three-nodal net represented by the Schläfli symbol $(4\cdot8^2)(4\cdot8^8\cdot10)(8)$.

Comment

The design and synthesis of coordination polymers have attracted great attention not only for their impressive structural diversity, but also for their potential applications as functional materials in molecular adsorption, chemical separation, heterogeneous catalysis, ion exchange, drug delivery, magnetism and photoluminescence (Mueller *et al.*, 2006; McKinlay *et al.*, 2010; Kurmoo, 2009; Allendorf *et al.*, 2009). To construct such materials, the rational design of a suitable organic linker is one of the various factors to be taken into account. From a crystal engineering point of view, the ligand should be: (i) multidentate; (ii) structurally predisposed for extending the metal ions in different directions in order to form a multidimensional coordination network; (iii) relatively rigid allowing for a certain control of the steric consequences in the assembly process. Dinicotinic acid (pyridine-3,5-dicarboxylic acid) appears to be an interesting ligand because of the strong binding ability and versatile coordination modes of the functional groups. A search of the Cambridge Structural Database (CSD, Version 5.32; Allen, 2002) has revealed that dinicotinic acid has been widely used to form inorganic–organic hybrid compounds with the main group metal ions Na^+ (one compound), Ca^{2+} (three), Sr^{2+} (one), Ba^{2+} (one), In^{3+} (two), Tl^+ (one), Sn^{4+} (three) and Pb^{2+} (one), as well as with transition metals (49) and rare earth metal ions (25). It has also been used as a ligand in 19 heterobimetallic metal–organic frameworks (MOFs). On the other hand, the phosphonic analogue of dinicotinic acid, namely (pyridine-3,5-diyl)diphosphonic acid, is geometrically and topochemically predisposed for binding and extending metal ions in different, not necessarily planar, directions, forming a great variety of diverse coordination modes, dependent upon the deprotonation rate and the metal–ligand ratio. However, to the best of our knowledge, (pyridine-3,5-diyl)diphosphonic acid has not been used previously as a linker to form coordination polymers. We report here the crystal structure of the first such example, poly[aqua[μ_3-(pyridin-1-ium-3,5-diyl)diphosphonato-κ^3O:O':O''][μ_2-(pyridin-1-ium-3,5-diyl)diphosphonato-κ^2O:O']calcium(II)], (I).



(I)

The asymmetric unit of (I) contains one Ca^{2+} ion, two symmetry-independent (pyridin-1-ium-3,5-diyl)diphosphonate monoanions and one coordinated water molecule. The Ca^{2+} ion is six-coordinate with a distorted octahedral geometry. The coordination environment of the metal ion consists of five phosphonate O atoms located on five different (pyridin-1-ium-3,5-diyl)diphosphonate ligands, two of which are unique, and one water O atom (Fig. 1). Atoms $O14^i$, $O21^{ii}$, O22 and $O25^{iii}$ bind four ligands in one coordination plane around the Ca^{2+} ion, while O11 and O1*W* coordinate per-

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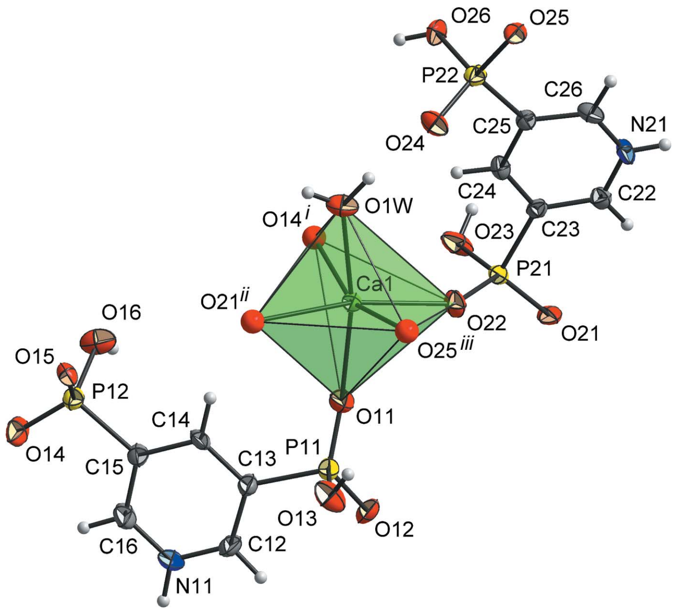

Figure 1
The asymmetric unit and the coordination polyhedron of (I), together with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes are as in Table 1.

pendicular to that plane. The Ca—O bond lengths are in the range 2.280 (2)–2.450 (3) Å (symmetry codes as in Table 1).

Two singly ionized (pyridin-1-ium-3,5-diyl)diphosphonate moieties having a zwitterion form, *L*1 and *L*2, serve as $\eta^2\mu_2$ and $\eta^3\mu_3$ ligands, respectively, to extend the Ca^{2+} ions into a three-dimensional framework. Each ligand uses both phosphonate sites to bind in a monodentate manner to the Ca^{2+} ions, linking them into *C*1,2(8) helical chains along the *b* axis (Videnova-Adrabinska, 2007). Another O-atom site from one of the phosphonate groups in *L*2 is used to bridge metal ions from Ca–*L*2 helices aligned in the opposite direction, thus interweaving them into a two-dimensional coordination network *via* a 16-membered *R*2,4(16) ring, closed between two metal centres, two pyridine rings and four phosphonate groups. The Ca–*L*2 framework involves a large *R*4,8(24) motif, generated and located between four metal ions, two pyridine rings and six phosphonate groups (Fig. 2*a*). The Ca–*L*2 network is strongly folded and the pyridine rings, acting as linkers between the phosphonate sites, are tilted at an angle of 35.22 (10)° toward the mean *bc* plane of the framework. The folding of the two-dimensional network is supported by a pyridine–phosphonate hydrogen bond, *viz*. N21—H21$\cdots$O25^{v} (symmetry code as in Table 2), established between the protonated N atom and the phosphonate O-atom site of adjacent glide-related monoanions and offset face-to-face (OFF) interactions established between neighbouring inversion-related pyridine rings [$Cg2\cdots Cg2^{viii}$ = 3.6861 (19) Å (*Cg* is the ring centroid in *L*2) and slippage = 1.208 Å; symmetry

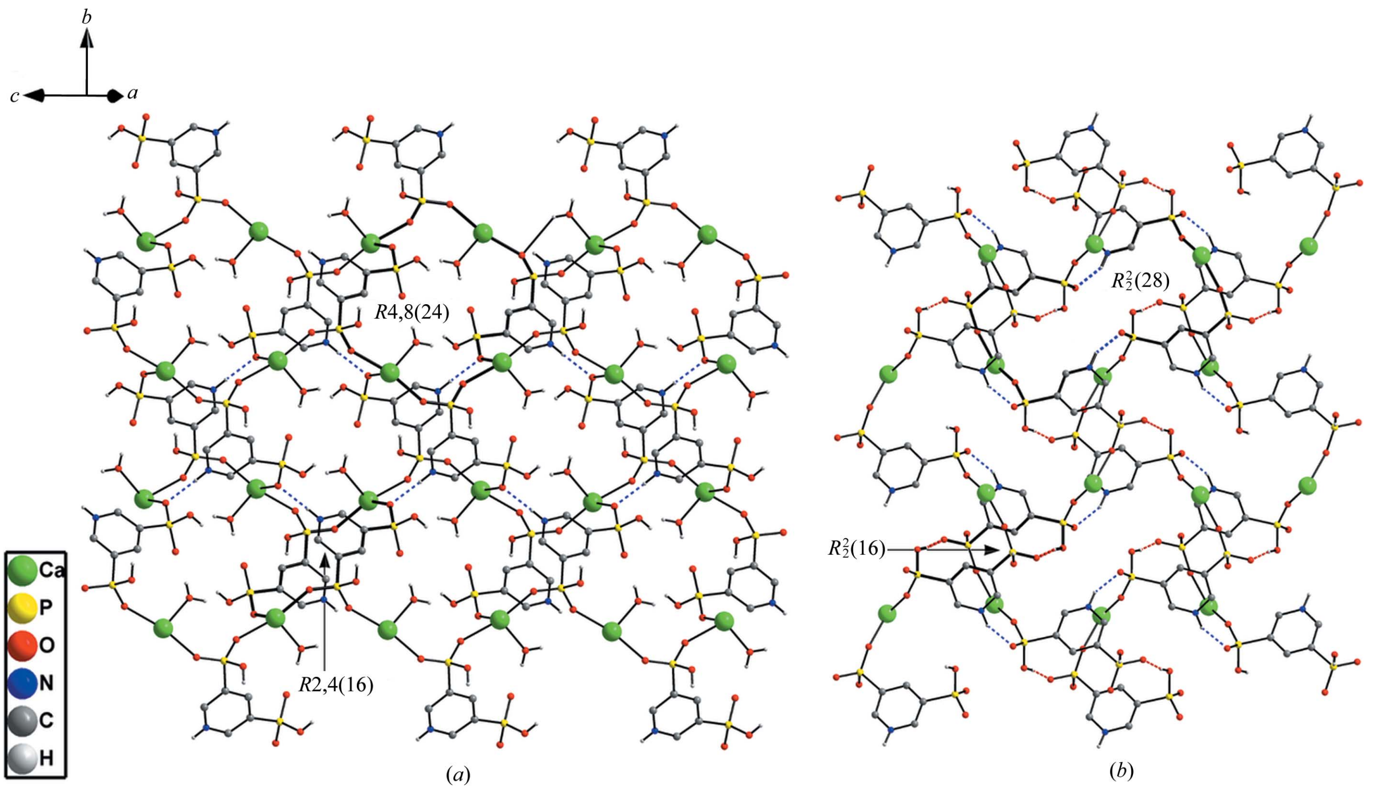

Figure 2
The disentangled frameworks formed by the two unique ligands *L*1 and *L*2. (*a*) A view of the two-dimensional Ca–*L*2 coordination framework, together with the folding N—H$\cdots$O hydrogen bonds. The stabilizing O—H$\cdots$O hydrogen bonds have been omitted for clarity. (*b*) A view of four Ca–*L*1 helical chains interconnected *via* N—H$\cdots$O and O—H$\cdots$O hydrogen bonds, drawn as dashed lines (in the electronic version of the paper, blue for N—H$\cdots$O and red for O—H$\cdots$O). The pyridine (C)H atoms have been omitted for clarity.

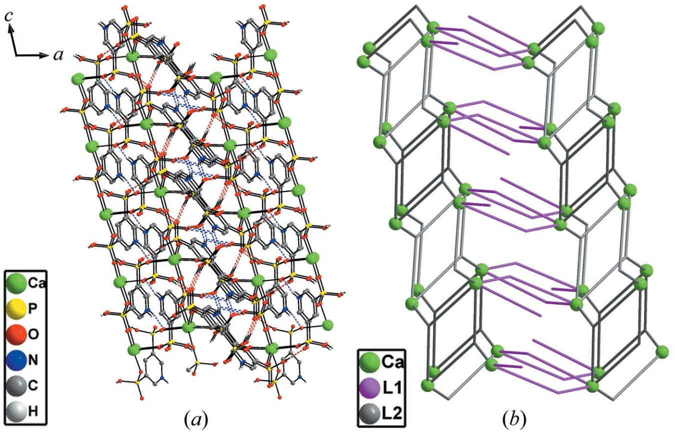

Figure 3
(*a*) A view of the three-dimensional coordination framework. The *L*1–*L*1 (O16—H16O···O12^{vi} and N11—H11···O15^{vii}), *L*2–*L*2 (N21—H21···O25^{v}) and *L*1–*L*2 (O23—H23O···O15^{iv}, O26—H26O···O12^{ii}, O13—H13O···O24^{iii} and N11—H11···O23^{vi}) hydrogen bonds are drawn as dashed lines. The terminal aqua ligands and the pyridine (C)H atoms have been omitted. Symmetry codes are as given in Table 2. (*b*) A schematic presentation of the three-dimensional (2,3,5)-connected net with $(4{\cdot}8^2)(4{\cdot}8^8{\cdot}10)(8)$ topology.

code: (viii) $-x + 2, -y + 1, -z$]. The aqua ligand, completing the coordination environment of the Ca^{2+} ion, is arranged in the *R*4,8(24) ring and donates two water–phosphonate hydrogen bonds, *viz.* O1*W*—H1*W*···O24 and O1*W*—H2*W*···O22^{ii} (symmetry code as in Table 2), which additionally stabilize the Ca–*L*2 framework.

The other acid monoanion, *L*1, connects the Ca^{2+} ions in a $\eta^2\mu_2$ fashion, forming a one-dimensional helical *C*1,2(8) chain along the *b* axis (Fig. 2*b*). Neighbouring Ca–*L*1 helices are linked together by two different hydrogen bonds to create a two-dimensional hydrogen-bonded network parallel to the crystallographic *bc* plane. The first hydrogen bond, O16—H16O···O12^{vi} (symmetry code as in Table 2), is established between phosphonate O-atom sites of adjacent inversion-related monodeprotonated ligands and forms an $R_2^2(16)$ hydrogen-bonded ring motif. The second hydrogen bond, N11—H11···O15^{vii} (symmetry code as in Table 2), is established between the protonated N atom and a phosphonate O-atom site of a neighbouring glide-related monoanion and serves to form an $R_2^2(28)$ hydrogen-bonded ring motif.

The Ca–*L*1 helical chains and the Ca–*L*2 network are interweaved at the metal ions in order to form a three-dimensional framework. Three phosphonate–phosphonate hydrogen-bond interactions, *viz.* O23—H23O···O15^{iv}, O26—H26O···O12^{ii} and O13—H13O···O24^{iii}, and a pyridine–phosphonate hydrogen bond, *viz.* N11—H11···O23^{vi} (symmetry codes as in Table 2), established between the two different *L*1 and *L*2 ligands, stabilize the crystal framework.

However, the three-dimensional packing pattern of the compound can also be portrayed as a pillared bilayer structure. The *L*2 ligands are arranged in the interior and the Ca^{2+} ions on the surfaces of the bilayers. The *L*1 ligands serve to connect the layers and act as pillars between them (Fig. 3*a*).

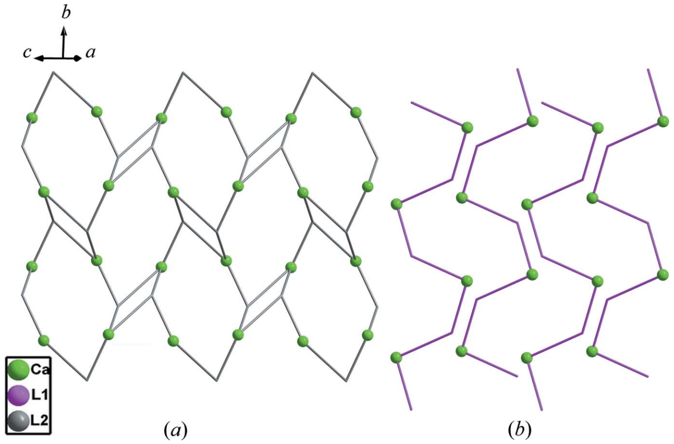

Figure 4
A topological presentation of the simplified coordination frameworks (*a*) Ca–*L*2 and (*b*) Ca–*L*1.

To get a better insight into the nature of the intricate coordination framework one can apply the topological approach, which permits a description of multidimensional structures in terms of simple node-and-linker nets. One can consider the Ca^{2+} ion as a five-connected node (the terminal aqua ligand is disregarded during the simplification process) and the *L*1 and *L*2 ligands as two- and three-connected linkers (Figs. 4*a* and 4*b*). Hence, the three-dimensional network of (I) will be presented as a three-nodal (2,3,5)-connected net expressed by the Schläfli symbol $(4{\cdot}8^2)(4{\cdot}8^8{\cdot}10)(8)$ (Fig. 3*b*) (Blatov, 2006). To the best of our knowledge, this is a new type of network.

In summary, a novel three-dimensional coordination polymer, (I), featuring a unique $(4{\cdot}8^2)(4{\cdot}8^8{\cdot}10)(8)$ topology is presented. It demonstrates an alternate arrangement of two-dimensional Ca–*L*2 frameworks and one-dimensional Ca–*L*1 helical chains that interweave at the metal ions. To the best of our knowledge, (I) is the first coordination polymer based on a phosphonic analogue of pyridine-3,5-dicarboxylic acid. To date, only three crystal structures of calcium complexes with the dinicotinate ligand have been reported. These are the zero-dimensional ionic complex $[Ca_2(C_7H_4NO_4)_3(H_2O)_9]$-$(C_7H_4NO_4)\cdot 2H_2O$ (Starosta *et al.*, 2003), the zero-dimensional dinuclear complex $[Ca_2(C_7H_3NO_4)_2(H_2O)_{10}]\cdot 2H_2O$ (Starosta *et al.*, 2002*a*) and the one-dimensional zigzag chain structure $[Ca(C_7H_3NO_4)(H_2O)_5]_n$ (Starosta *et al.*, 2002*b*).

Experimental

All chemicals were obtained commercially, with the exception of (pyridine-3,5-diyl)diphosphonic acid which was prepared according to a published procedure (Zon *et al.*, 2011). The title compound was synthesized by mixing calcium(II) nitrate tetrahydrate (15 mg, 0.06 mmol) dissolved in distilled water (0.5 ml) with (pyridine-3,5-diyl)diphosphonic acid (30 mg, 0.12 mmol) also dissolved in distilled water (2 ml). The resulting solution was placed in a tightly closed tube and heated at 348 K for 2 d. The mixture was then cooled to room temperature and colourless parallelepiped-shaped crystals of (I) of sufficient quality for X-ray diffraction were grown.

Crystal data

$[Ca(C_5H_6NO_6P_2)_2(H_2O)]$
$M_r = 534.19$
Monoclinic, $P2_1/c$
$a = 12.296$ (2) Å
$b = 13.054$ (3) Å
$c = 12.308$ (3) Å
$\beta = 101.33$ (1)°
$V = 1937.0$ (8) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.73$ mm^{-1}
$T = 295$ K
0.28 × 0.22 × 0.18 mm

Data collection

Kuma KM-4 diffractometer with CCD area detector
Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{\min} = 0.824$, $T_{\max} = 0.882$
24330 measured reflections
4673 independent reflections
2710 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.084$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.063$
$S = 0.99$
4976 reflections
295 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Ca1—O14^{i}	2.280 (2)	P12—O14	1.483 (2)
Ca1—O11	2.298 (2)	P12—O15	1.500 (2)
Ca1—O21^{ii}	2.312 (2)	P12—O16	1.556 (2)
Ca1—O22	2.324 (2)	P21—O21	1.482 (2)
Ca1—O25^{iii}	2.363 (2)	P21—O22	1.488 (2)
Ca1—O1*W*	2.450 (3)	P21—O23	1.558 (2)
P11—O11	1.473 (2)	P22—O24	1.497 (2)
P11—O12	1.508 (2)	P22—O25	1.501 (2)
P11—O13	1.553 (3)	P22—O26	1.557 (2)

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$.

The positions of H atoms attached to pyridine C atoms were constrained (C—H = 0.93 Å), with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. The positions of H atoms involved in hydrogen bonds were refined with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm O})$ or $1.2U_{\rm eq}({\rm N})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2008); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O24	0.87 (4)	1.94 (4)	2.800 (3)	174 (4)
O1*W*—H2*W*···O22^{ii}	0.81 (3)	2.55 (4)	3.218 (3)	140 (4)
O23—H23O···O15^{iv}	0.87 (3)	1.65 (3)	2.515 (3)	172 (4)
O26—H26O···O12^{ii}	0.81 (3)	1.73 (3)	2.536 (3)	171 (4)
N21—H21···O25^{v}	0.84 (3)	1.92 (3)	2.749 (3)	169 (3)
O13—H13O···O24^{iii}	0.88 (4)	1.68 (4)	2.550 (3)	168 (4)
O16—H16O···O12^{vi}	0.87 (3)	1.72 (3)	2.584 (3)	170 (4)
N11—H11···O15^{vii}	0.95 (3)	1.81 (3)	2.668 (4)	149 (3)
N11—H11···O23^{vi}	0.95 (3)	2.57 (3)	3.137 (4)	119 (2)

Symmetry codes: (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (v) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (vi) $-x+1, -y, -z$; (vii) $x, -y-\frac{1}{2}, z-\frac{1}{2}$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3267). Services for accessing these data are described at the back of the journal.

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