Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

catena-Poly[[[tetrakis(dimethylformamide-κ*O*)-magnesium(II)]-μ-diphenylphosphato-κ^2*O*:*O*′] trifluoromethanesulfonate]

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Received 12 May 2005
Accepted 26 May 2005
Online 10 June 2005

Key indicators

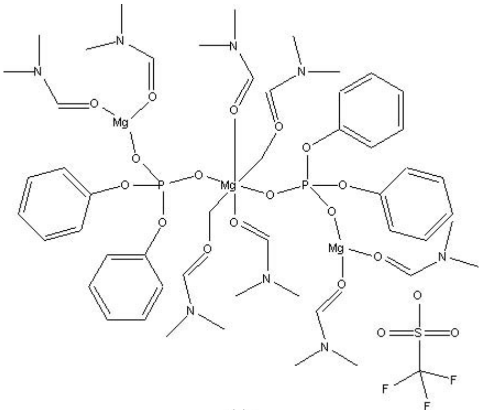
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.045
wR factor = 0.119
Data-to-parameter ratio = 13.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Mg(C_{12}H_{10}O_4P)(C_3H_7NO)_4](CF_3O_3S)$, consists of diphenylphosphate anions linked into infinite chains by bridging magnesium ions, which are also coordinated by dimethylformamide molecules. A non-coordinated trifluoromethanesulfonate counter-ion provides charge balance. Both crystallographically distinct magnesium cations occupy special positions with $\overline{1}$ site symmetry.

Comment

There are few examples of phosphodiester molecules that are linked by magnesium ions (Cremlyn *et al.*, 1958; Ezra & Collin, 1973; Schwalbe *et al.*, 1973). Narayan *et al.* (1978) described an unusual crystal structure in which phosphodiester anions are linked by magnesium cations into a chain structure. This compound arose from the crystallization of magnesium diphenylphosphate in moist diethyl ether.



(I)

The related title compound, (I), arose from the attempted crystallization of an imidazole catalyst intermediate. The asymmeric unit of (I) (Fig. 1) contains one diphenylphosphate anion, four distinct dimethylformamide (DMF) molecules, one non-coordinated trifluoromethanesulfonate counter-ion and two crystallographically distinct octahedrally coordinated (Table 1) magnesium cations (both with site symmetry $\overline{1}$). The main differences between the structures are that (I) has DMF coordinated to Mg, whereas the Narayan *et al.* (1978) compound has water molecules. In the Narayan structure, four phosphate O atoms and two water molecules are coordinated to each Mg atom, whereas in (I), two phosphate O atoms and four DMF O atoms link to each Mg atom (Fig. 2). In the Narayan structure, the mean $Mg-O_P$ (P = phosphate) and $Mg-O_W$ (W = water) bond distances are 2.042 (4) and 2.154 (4) Å, respectively. Equivalent values of 2.0491 (18) and 2.075 (19) Å [for $Mg-O_D$ (D = DMF)] arise in (I). The

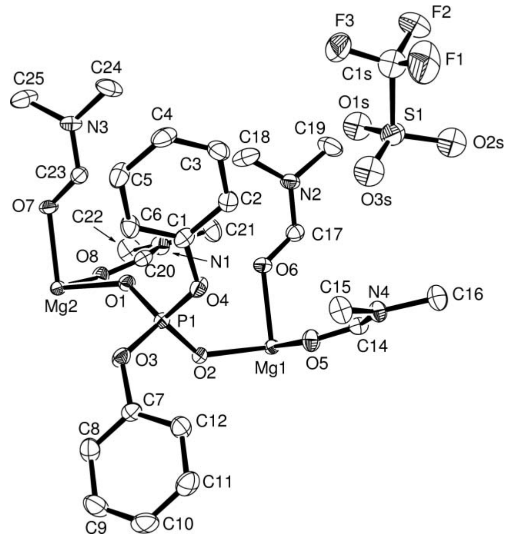


Figure 1
The asymmetic unit of (I), with displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

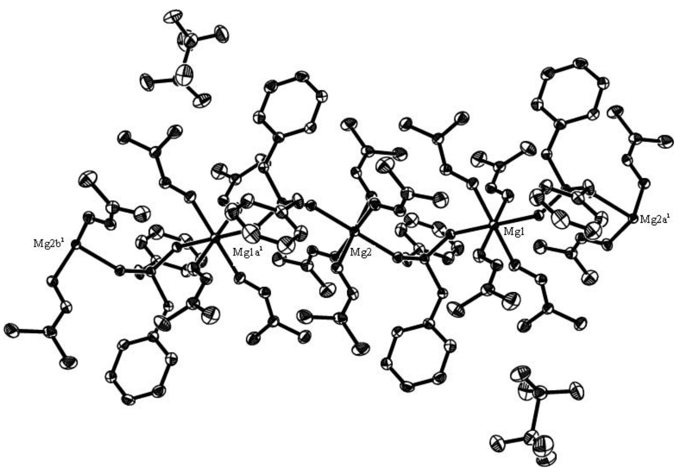


Figure 2
An extended view of the chain structure of (I) [symmetry code: (i) $-x$, $-y + 2$, $-z$]. H atoms have been omitted for clarity.

phosphorus–phenyl bond lengths are comparable in both structures. There appear to be no significant hydrogen-bonding intractions in (I).

Experimental

A solution of diphenyl chlorophosphate (0.319 g, 0.118 mmol), 2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxymethyl}-1-methyl-1*H*-imidazole (0.25 g, 0.118 mmol), and magnesium trifluoromethanesulfonate (0.038 g, 0.118 mmol) in dry DMF (5 ml) in a specimen vial was submersed into a sealed specimen vial containing dry diethyl ether (5 ml). This was kept for 4 d at 283 K to allow slow growth of crystals. Once harvested, the crystals of (I) were very sensitive to atmospheric moisture and were prone decomposition whilst being handled.

Crystal data

$[Mg(C_{12}H_{10}O_4P)(C_3H_7NO)_4]$-$(CF_3O_3S)$
$M_r = 714.93$
Triclinic, $P\overline{1}$
$a = 11.2645$ (19) Å
$b = 11.4907$ (19) Å
$c = 13.665$ (2) Å
$\alpha = 95.865$ (3)°
$\beta = 104.109$ (3)°
$\gamma = 100.969$ (3)°
$V = 1663.4$ (5) Å^3
$Z = 2$
$D_x = 1.427$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 139 reflections
$\theta = 7.3$–50.6°
$\mu = 0.24$ mm^{-1}
$T = 150$ (2) K
Block, colourless
0.48 × 0.32 × 0.21 mm

Data collection

Bruker SMART1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min} = 0.893$, $T_{max} = 0.951$
11079 measured reflections
5729 independent reflections
4183 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 25.0°$
$h = -13 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.119$
$S = 1.01$
5729 reflections
426 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 1.6348P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mg1—O2	2.0532 (18)	Mg2—O1	2.0491 (18)
Mg1—O5	2.061 (2)	Mg2—O8	2.0695 (19)
Mg1—O6	2.0898 (18)	Mg2—O7	2.0808 (18)
P1—O1—Mg2	136.79 (11)	P1—O2—Mg1	136.67 (11)

H atoms were positioned geometrically, with C—H = 0.95–0.98 Å, and refined as riding (including torsional freedom for methyl groups) with the constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) or $1.5U_{eq}$(methyl carrier).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

EPSRC and Onyx Scientific for funding (AR).

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m1252 Adams *et al.* • $[Mg(C_{12}H_{10}O_4P)(C_3H_7NO)_4](CF_3O_3S)$ *Acta Cryst.* (2005). E**61**, m1251–m1252