Crystal structure of (dimethylphosphoryl)methanaminium hydrogensulfate, $C_3H_{12}NO_5PS$

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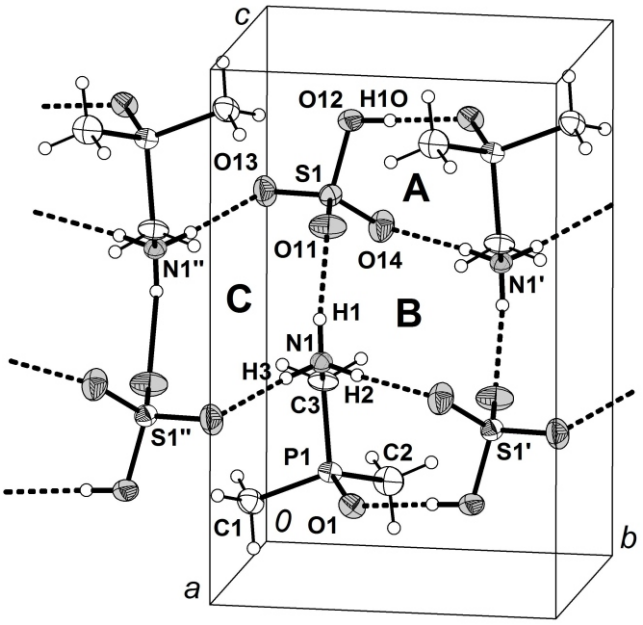

Abstract

$C_3H_{12}NO_5PS$, triclinic, $P\bar{1}$ (no. 2), a = 5.9356(1) Å, b = 6.8650(1) Å, c = 10.6318(2) Å, α = 92.2821(13)°, β = 98.5671(13)°, γ = 100.8764(14)°, V = 419.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.0262, $wR_{ref}(F^2)$ = 0.0595, T = 290 K.

Table 1. Data collection and handling.

Crystal:	colourless irregular, size 0.21 0.30 0.48 mm
Wavelength:	Mo K radiation (0.71073 Å)
μ:	5.56 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Eos, ω
$2\theta_{max}$:	70°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	51992, 3688
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3317
$N(param)_{refined}$:	118
Programs:	CrysalisPRO [1], SHELX [2], DIAMOND [3]

Source of material

In a typical reaction, 1.11 g (10.37 mmol) (dimethylphosphoryl)-methanamine (*dpma*) were dissolved in 3 ml concentrated sulfuric acid by heating up the mixture. After the recrystallization from an acetone/water mixture, colourless needles formed upon slow cooling to room temperature. **IR spectra** were measured at room temperature on an Excalibur FTS 3500 spectrometer (Digilab, Germany) with an apodized resolution of 2 cm^{-1} using a MIRacle ATR unit (Pike technologies, Madison, USA) in the region of 4000-530cm^{-1}: 3399(*m*), 3265(*m*), 3167(*s*), 2997(*s*), 2918(*s*), 2884(*s*), 2814(*s*), 2675(*m*), 2575(*m*), 2070(*w*), 1625(*m*), 1545(*w*), 1498(*m*), 1422(*w*), 1374(*w*), 1308(*m*), 1298(*m*), 1156(*s*), 1125(*s*), 1061(*s*), 1013(*s*), 944(*s*), 912(*m*), 880(*s*), 770(*m*), 732(*m*), 652(*w*), 596(*m*), 579(*m*). **Raman spectra** were recorded on a MultiRam spectrometer (Bruker Optics, Germany) with an apodized resolution of 8 cm^{-1} equipped with a Nd-YAG laser: 1064 nm and a RT-InGaAS-detector (4000–70 cm^{-1}): 3245(*w*), 3160(*w*), 2998(*s*), 2970(*m*), 2921(*s*), 2848(*w*), 2818(*w*), 2595(*w*), 1620(*w*), 1507(*w*), 1408(*w*), 1419(*w*), 1431(*w*), 1332(*w*), 1309(*w*), 1166(*w*), 1127(*w*), 1071(*w*), 1022(*m*), 1008(*m, sh*), 973(*w*), 951(*w*), 913(*w*), 883(*w*), 858(*w*), 771(*w*), 754(*w*), 732(*m*), 652(*s*), 587(*w*), 444(*w*), 421(*w*), 390(*w*), 316(*w*), 278(*w*), 253(*w*), 217(*w*).

Experimental details

All hydrogens were located in successive difference Fourier maps. In the final stages of the refinement the two methyl groups and the methylene group are included using a riding model with the U_{iso} values set to 1.5U_{eq}(C_{methyl}) and 1.2U_{eq}($C_{methylene}$). The coordinates of the hydrogen atoms involved in hydrogen bonds were refined freely together with individually refined U_{iso} values.

Discussion

The ability of the bidentate (dimethylphosphoryl)methanamine (*dpma*) ligand to coordinate various metal centers has already been shown [4-8]. The syntheses and structures of some *dpma*H$^+$ salts were subjects of recent investigations [9-13]. Furthermore, the *dpma*H$^+$ cation can act as a monodentate ligand to form cationic transition metal complexe [14, 15].

The asymmetric unit of the title structure *dpma*H[HSO_4] consists of one *dpma*H$^+$ cation and one hydrogensulfate anion both in general positions. The geometrical parameters of the *dpma*H$^+$ cation and the [HSO_4]$^-$ anion are as expected. The *dpma*H$^+$ tecton features a threefold hydrogen bond donor group at one end (NH_3^+) and a single hydrogen bond accepting –P=O group at the other end. Most of the structurally characterized *dpma*H$^+$ salts show a head-to-tail connection of two or more *dpma*H$^+$ tectons leading to dimers or polymers [9, 11-13]. So far, only in the structure of the (H_3O)(*dpma*H)$_2$Br$_3$ [10] no head-to-tail connection is present [10]. Similarily to this latter example, in the title structure each *dpma*H$^+$ cation is connected to three hydrogensulfate anions by three medium strong, charge supported NH$^+$···O=S- hydrogen bonds (N···O: 2.7948(13)-2.8832(13) Å, dashed lines in the figure) and one strong OH···O=P- hydrogen bond (O···O = 2.5143(11) Å, dashed line in the figure) [16]. Consequently, each anion is surrounded by three cations. The three resulting crystallographically different ring systems (indicated by A, B and C in the figure) can be classified by the following second level graph-

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set descriptors: A: $R^2_2(9)$; B: $R^4_4(12)$; C: $R^4_4(12)$ [17]. A polymeric strand structure which runs along [010] is formed by these connections. This structure is a further example for the suitability of the *dpma*H^+ cation to form hydrogen bonded one-dimensional structures [9,11-15].

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	2*i*	0.653(3)	0.261(2)	0.499(2)	0.043(4)
H(2)	2*i*	0.733(3)	0.382(2)	0.407(1)	0.040(4)
H(3)	2*i*	0.727(3)	0.175(2)	0.395(2)	0.046(4)
H(1O)	2*i*	0.291(3)	0.404(3)	0.832(2)	0.068(6)
H(1A)	2*i*	0.2620	0.0068	0.0178	0.052
H(1B)	2*i*	0.1503	0.0597	0.1378	0.052
H(1C)	2*i*	0.4091	0.0738	0.1318	0.052
H(2A)	2*i*	0.1985	0.5096	0.1843	0.061
H(2B)	2*i*	0.0169	0.3087	0.1668	0.061
H(2C)	2*i*	0.1305	0.3909	0.0507	0.061
H(3A)	2*i*	0.3339	0.3284	0.3890	0.041
H(3B)	2*i*	0.3319	0.1004	0.3714	0.041

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	2*i*	0.38435(4)	0.24760(4)	0.18115(2)	0.01754(9)	0.0301(1)	0.0224(1)	0.00369(8)	0.00324(7)	0.00019(8)
N(1)	2*i*	0.6545(2)	0.2653(1)	0.41894(9)	0.0284(4)	0.0296(4)	0.0236(4)	0.0040(3)	0.0002(3)	0.0019(3)
O(1)	2*i*	0.6130(1)	0.3483(1)	0.14749(8)	0.0223(3)	0.0349(4)	0.0343(4)	0.0004(3)	0.0096(3)	0.0018(3)
S(1)	2*i*	0.21603(4)	0.22012(4)	0.67822(2)	0.0243(1)	0.0264(1)	0.0259(1)	0.00277(8)	0.00407(8)	0.00283(8)
O(11)	2*i*	0.4504(2)	0.2503(2)	0.64827(9)	0.0297(4)	0.0714(7)	0.0341(4)	0.0022(4)	0.0130(3)	0.0034(4)
O(12)	2*i*	0.2377(2)	0.2823(1)	0.82221(8)	0.0434(4)	0.0324(4)	0.0271(3)	0.0021(3)	0.0122(3)	0.0030(3)
O(13)	2*i*	0.1041(2)	0.0124(1)	0.66728(9)	0.0451(5)	0.0254(3)	0.0514(5)	0.0011(3)	0.0132(4)	0.0017(3)
O(14)	2*i*	0.0793(2)	0.3455(1)	0.60759(9)	0.0464(5)	0.0351(4)	0.0453(5)	0.0107(4)	0.0131(4)	0.0036(4)
C(1)	2*i*	0.2907(2)	0.0020(2)	0.1088(1)	0.0328(5)	0.0341(5)	0.0332(5)	0.0004(4)	0.0051(4)	0.0033(4)
C(2)	2*i*	0.1564(2)	0.3793(2)	0.1412(1)	0.0305(5)	0.0526(7)	0.0429(6)	0.0194(5)	0.0044(4)	0.0046(5)
C(3)	2*i*	0.4110(2)	0.2311(2)	0.3540(1)	0.0240(4)	0.0541(7)	0.0239(4)	0.0031(4)	0.0051(3)	0.0000(4)

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