

## Hydrogen bonding in bis(triphenylphosphine-*P*)iminium hydrogensulfate chloroform solvate

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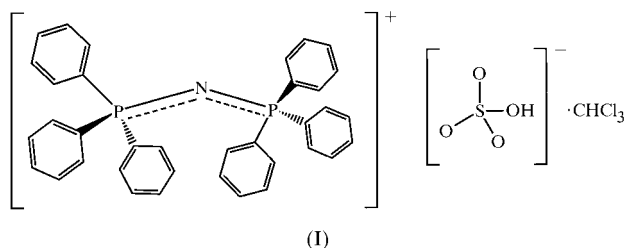
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The title compound,  $C_{36}H_{30}NP_2^+ \cdot HSO_4^- \cdot CHCl_3$ , consists of discrete ions and well separated chloroform solvate molecules. The central feature of the structure is O–H···O hydrogen bonding between two hydrogensulfate ions related by a crystallographic inversion centre. The chloroform solvate molecule takes part in a well defined C–H···O hydrogen bond.

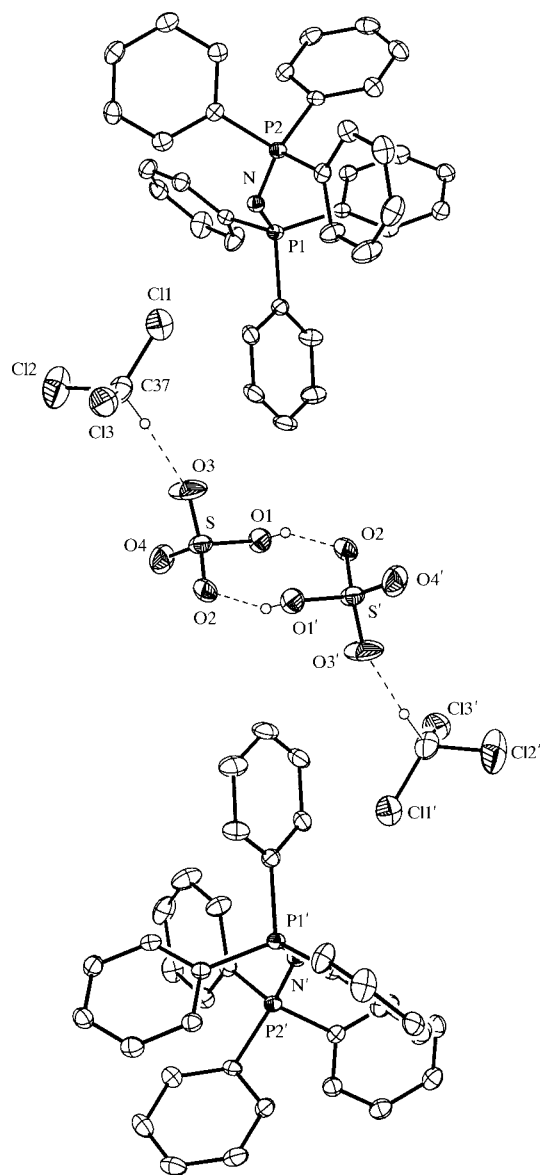
### Comment

We report herein the structure of  $[Ph_3P=N=PPh_3]^+ [HSO_4]^- \cdot CHCl_3$ , (I), isolated from chloroform and heptane as a by-product of the recrystallization of  $(PPN)[Re_3Cl_9(SO_4)]$  [PPN is bis(triphenylphosphine)iminium], which was prepared from the reaction of  $(Re_3Cl_9)_x$ , PPNCl and  $H_2SO_4$  in water.



The structure of (I) consists of discrete ions and well separated chloroform solvate molecules. The location of the H atom on O1 of the hydrogensulfate anion is unequivocal, as indicated by the longer S–O1 distance [1.541 (3) Å] compared with the other S–O bond lengths [average 1.428 (11) Å]. In 30 hydrogensulfate ions reported to the Cambridge Structural Database (CSD; Allen & Kennard, 1993), the corresponding values averaged 1.53 (3) and 1.43 (2) Å, respectively. The central feature of the structure is hydrogen bonding between two hydrogensulfate ions related by a crystallographic inversion centre (Fig. 1). Due to the symmetry considerations, both hydrogen bonds have identical parameters. The O1···O2(1 – x, 2 – y, 1 – z) distance is 2.633 (4) Å, while the O–H···O angle is 155°. The corresponding values for 23 similar  $HSO_4^-$ – $HSO_4^-$  hydrogen-

bonding interactions in structures reported to the CSD were 2.58 (4) Å and 164 (10)°. The only structure with two symmetrical hydrogen bonds between two hydrogensulfate moieties [average O···O separation 2.63 (1) Å and O–H···O angle 150 (2)°] was reported for  $[Fe(TTP)(HSO_4)] \cdot 0.5C_6H_6$  (TTP is tetraphenylporphinate; Scheidt *et al.*, 1988). In addition, the chloroform solvate forms a weak but well defined hydrogen bond to the sulfate anion, C37–H37···O3(–x +  $\frac{3}{2}$ , y –  $\frac{1}{2}$ ,  $\frac{1}{2}$  – z). The C···O separation was found to be 2.990 (7) Å, while the C–H···O angle measured 174°. The environment about the S atom is distorted tetrahedral, with the O–S–O angles ranging from 105.38 (19) to 113.5 (3)°. The  $[Ph_3P=N=PPh_3]^+$  cation is rather typical. The P–N distance [average 1.589 (3) Å] is slightly longer than the P=N distance of 1.576 (18) Å obtained by averaging 562 P–N



**Figure 1**  
The structure of (I) showing hydrogen bonds between symmetry-related species. The displacement ellipsoids are shown at the 30% probability level.

distances in PPN<sup>+</sup> ions reported to the CSD. The P—N—P angle in (I) [134.42 (19)<sup>o</sup>] is noticeably smaller than the average angle of 143 (8)<sup>o</sup> found in the same 562 PPN<sup>+</sup> cations in the CSD. The large s.u.'s calculated for the two parameters for complexes reported to the CSD reveal that the geometry about the N atom in PPN<sup>+</sup> ions may vary substantially. Both P atoms in (I) are tetrahedral, with the average C—P—C and C—P—N angles averaging 109 (3)<sup>o</sup>.

## Experimental

### Crystal data

C<sub>36</sub>H<sub>30</sub>NP<sub>2</sub><sup>+</sup>·HSO<sub>4</sub><sup>-</sup>·CHCl<sub>3</sub>  
M<sub>r</sub> = 754.99

Monoclinic, P2<sub>1</sub>/n  
a = 15.3399 (13) Å  
b = 16.2211 (13) Å  
c = 15.6888 (13) Å  
β = 113.1010 (10)<sup>o</sup>  
V = 3590.8 (5) Å<sup>3</sup>  
Z = 4

D<sub>x</sub> = 1.397 Mg m<sup>-3</sup>  
Mo Kα radiation  
Cell parameters from 4430 reflections  
θ = 2–26<sup>o</sup>  
μ = 0.44 mm<sup>-1</sup>  
T = 173 (2) K  
Prism, colorless  
0.43 × 0.20 × 0.20 mm

### Data collection

Siemens CCD area-detector diffractometer  
φ and ω scans  
Absorption correction: empirical (SADABS; Blessing, 1995)  
T<sub>min</sub> = 0.832, T<sub>max</sub> = 0.917  
27 441 measured reflections

6269 independent reflections  
4010 reflections with I > 2σ(I)  
R<sub>int</sub> = 0.058  
θ<sub>max</sub> = 25.0<sup>o</sup>  
h = -18 → 16  
k = -19 → 19  
l = -18 → 18

### Refinement

Refinement on F<sup>2</sup>  
R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.061  
wR(F<sup>2</sup>) = 0.153  
S = 0.99  
6269 reflections  
434 parameters

H-atom parameters constrained  
w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.084P)<sup>2</sup>]  
where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3  
(Δ/σ)<sub>max</sub> = 0.001  
Δρ<sub>max</sub> = 0.45 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.42 e Å<sup>-3</sup>

**Table 1**

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...O2 <sup>i</sup>	0.84	1.85	2.633 (4)	155
C37—H37...O3 <sup>ii</sup>	1.00	1.99	2.990 (7)	174

Symmetry codes: (i) 1 - x, 2 - y, 1 - z; (ii)  $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$

Data collection: SMART (Siemens, 1996); cell refinement: SMART; data reduction: SHELXTL (Sheldrick, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1168). Services for accessing these data are described at the back of the journal.

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