Materials and Methods

All reagents were C. Erba RPE-ACS except $ZrOCl_2 \cdot 8H_2O$ which was a Merck "pro analysi" product. They were used without further purification.

The zirconium content of the materials was obtained by dissolving a weighed amount (about 150 mg) in a few drops of conc. HF, followed by precipitation with cupferron and subsequent calcination to ZrO_2.

Phosphate, chloride and fluoride anions were determined by Ion Chromatography. About 100 mg of sample was refluxed for 3 hours with 10 ml of 1M NaOH; after filtration and dilution, the solution was injected into a Dionex series 2000 i/sp instrument, using an IonPack AS4A column and a buffer solution, having the following composition : $1.7 \cdot 10^{-3}M$ in $NaHCO_3$, $1.8 \cdot 10^{-3}M$ in Na_2CO_3 ($3.5 \times 10^{-3}M$ in Na_2CO_3 for fluoride ions) as eluent.

Carbon and hydrogen elemental analysis was performed using a Carlo Erba 1106 Analyser.

XRD powder patterns were recorded with Cu Kα radiation on a Philips PW1710 automated powder diffractometer.

Synthesis Procedures

Microcrystalline γ-zirconium phosphate (particle size 0.5-2 μm) was prepared by the thermal decomposition of zirconium fluorocomplexes.[1]

$ZrPO_4Cl(CH_3)_2SO$ was prepared as follows:
1 g of γ-ZrP was dispersed in 50 ml of 5M HCl solution using dimethylsulfoxide (dmso) as solvent. The closed vessel was kept at 75°C for 48 hours. The solid was then separated from the dmso solution and contacted again following the same procedure. After this second contact, the separated solid was washed with ethanol and dried at 80°C. It was then stored over P_4O_{10}.

$ZrPO_4OH(H_2O) \cdot 3H_2O$ was obtained contacting 1 g of $ZrPO_4Cl(CH_3)_2SO$ with 350 ml of water for 48 hours at 20°C. The solid, separated from the solvent, was dried at 80°C and stored over NaCl saturated solution (75% relative humidity).

$ZrPO_4F(CH_3)_2SO$ was obtained as follows: 1 g of $ZrPO_4Cl(CH_3)_2SO$ was contacted twice with 110 ml of 0.03 M HF using dmso as solvent at 75°C for 3 days for each contact. The solid was then washed with water and dried at 80°C.

Procedure for the Determination of $S_{F/Cl}$

1 g of $ZrPO_4Cl(CH_3)_2SO$ (0.0033mol) was contacted with 350 ml of $5 \cdot 10^{-3}$ M HF (0.00175 mol) and maintained in a closed vessel for 4 days at 75°C under shaking. The separated solid was then washed with ethanol and dried at 80°C. The composition of the resulting material was $ZrPO_4Cl_{0.55}F_{0.45}(CH_3)_2SO$.

(1) Alberti, G.; Bernasconi, M. G.; Casciola, M. *Reactive Polym.* **1989**, *11,* 245.

X-ray data collection and Structure Solution

XRD powder patterns for structure determination of $ZrPO_4Cl(CH_3)_2SO$ were recorded according to the step scanning procedure (step size = 0.01°, counting time = 30s) in the range 6-120° 2theta with Cu Kα radiation on a Philips PW1710 diffractometer, PW1820 goniometer equipped with a bent graphite monochromator on the diffracted beam. A 0.25° divergence and scatter slit together with a 0.1mm receiving slit were used. The LFF tube operated at 50KV, 30mA. In order to minimise preferred orientations, that can easily occur in layered materials, the sample was carefully sideloaded on an aluminum sample holder with an oriented quartz monocrystal mounted on its back (supplied by The Gem Dugout, State College, PA).

A first determination of cell parameters was performed using the TREOR program.[2] For this, a preliminary peak-profile analysis for the determination of the position of Kα_1 maxima was carried out using the built-in Philips PC-APD routine. This program is able to separate Kα_1 and Kα_2 contributions and model the peak profile using a maximum of 15 parameters.

Indexation gave the following tetragonal cell : a=6.597 Å and c=10.245 Å as the best solution (M(20)=47).

Systematic extinctions were consistent with the space group P4/n. Integrated intensities on the range 13-120° 2theta were extracted by the "LeBail" full profile decomposition method with the use of the GSAS packet. The first reflection, at about 8.6° 2theta was excluded from the set because of its strong asymmetry. A Patterson map was then calculated, and all atoms of the asymmetric unit, except carbon atoms belonging to dmso, were located among the first 9 strongest peaks. This atomic set was easily positioned in the unit cell on the basis of symmetry and chemical composition.

A first Rietveld refinement was then performed by using GSAS again. Scale factor, background, zero shift, cell parameters and peak profile were refined at this stage. An Rwp value of 0.25 was reached. Difference Fourier maps did not reveal an unequivocal position for methyl groups. It was thus decided to locate them in their expected positions. At this stage, soft constraints on bond length and angles were also introduced. A statistic weight was applied and decreased during the refinement, until the last refinement cycles in which it was set at zero. The correct choice for methyl groups was confirmed by the increased stability of refinement and the Rwp value which rapidly decreased to 0.085, in later refinements. When the shifts in all parameters were less than their estimated standard deviations, it was decided to stop the refinement. All the atoms were refined isotropically; neutral atomic scattering factors were used. The shape of profile was modelled by a pseudo-Voight function in which a parameter for the asymmetry at low angle was included. A March-Dollase correction along the *0 0 l* direction was applied for preferred orientation.

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(2) Werner, P. E.; Eriksson, L.; Westdhal, M. *J. Appl. Crystallogr.* **1985**, *18*, 367.

Table S1 : Crystal data and refinement details for $ZrPO_4Cl(CH_3)_2SO$

Formula	$ZrPO_4Cl(CH_3)_2SO$
M	299.5
Crystal system	tetragonal
Space group	$P4/_n$
a/Å	6.5988(7)
c/Å	10.2478(4)
Z	2
$D_c/g \cdot cm^{-3}$	2.229
Pattern range, $2\theta/°$	13-120
Step scan increment, $2\theta/°$	0.01
Step scan time/s	30
N. of data	10725
N. of geometric observations	24
P-O distance, tolerance/Å	1.55, 0.03
Zr-O distance, tolerance/Å	2.00, 0.03
O···O distance for PO_4/Å	2.55, 0.03
O···O distance for ZrO_6/Å	2.90, 0.03
Zr-Cl	2.3, 0.05
O-S distance, tolerance/Å	1.55, 0.03
S-C	1.70, 0.03
N. of variables	34
R_p	0.066
R_{wp}	0.086
R_F	0.065

Table S2: Fractional atomic coordinates and isotropic thermal parameters for
ZrPO$_4$Cl(CH$_3$)$_2$SO

Atom	x (Å)	y (Å)	z (Å)	U_{iso} (Å^2)
Zr	.2500(0)	.2500(0)	.0912(9)	.00570
P	.2500(0)	.7500(0)	.0000(0)	.00106
O(S)	.2500(0)	.2500(0)	.8742(3)	.04606
O(P)	.2534(9)	.9386(7)	.0849(8)	.00894
Cl	.2500(0)	.2500(0)	.3297(6)	.06256
S	.2500(0)	.2500(0)	.7341(4)	.07648
C*	.0294(2)	.1962(1)	.6947(2)	.01763

* Occupancy 0.5

Table S3: Bond lengths (Å) and angles (°) for ZrPO$_4$Cl(CH$_3$)$_2$SO.

vector	length (Å)	angle	amplitude (°)
Zr-O(S)	2.2247	O(S)-Zr-O(P)	88.20
Zr-O(P)	2.0556	O(S)-Zr-Cl	180.00
Zr-Cl	2.4438	O(P)-Zr-O(P)[a]	89.94
P-O(P)	1.5195	O(P)-Zr-O(P)[a]	176.39
S-O(S)	1.4360	O(P)-P-O(P)[b]	110.07
S-C	1.5520	O(P)-P-O(P)[b]	109.17
		Zr-O(S)-S	180.00
		O(S)-S-C	105.16
		C-S-C[a]	86.11

[a] related by symmetry axis 4; [b] related by symmetry axis $\bar{4}$.
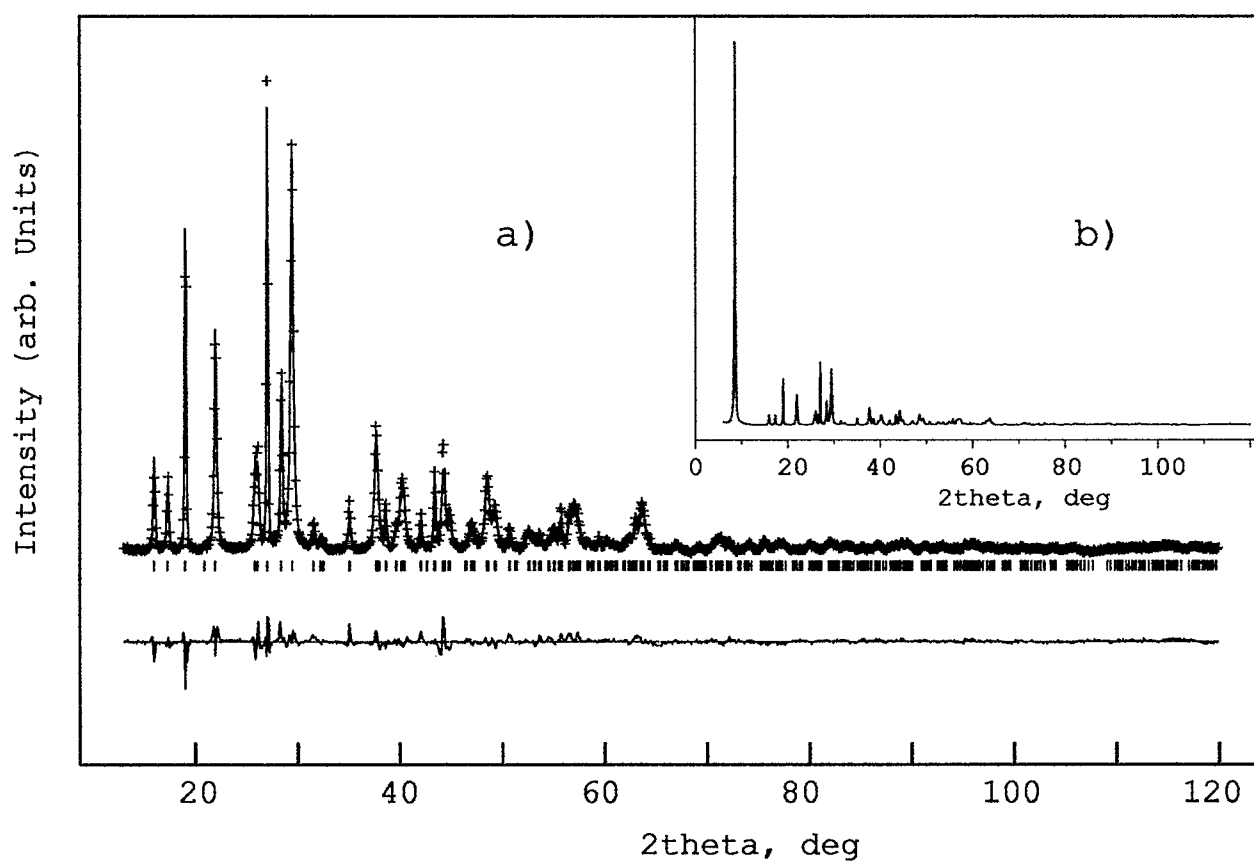
Figure S1: a) Observed (+) and calculated (solid line) XRD pattern for $ZrPO_4Cl(CH_3)_2SO$. Reflection markers and difference plot are at the bottom; b) experimental data.

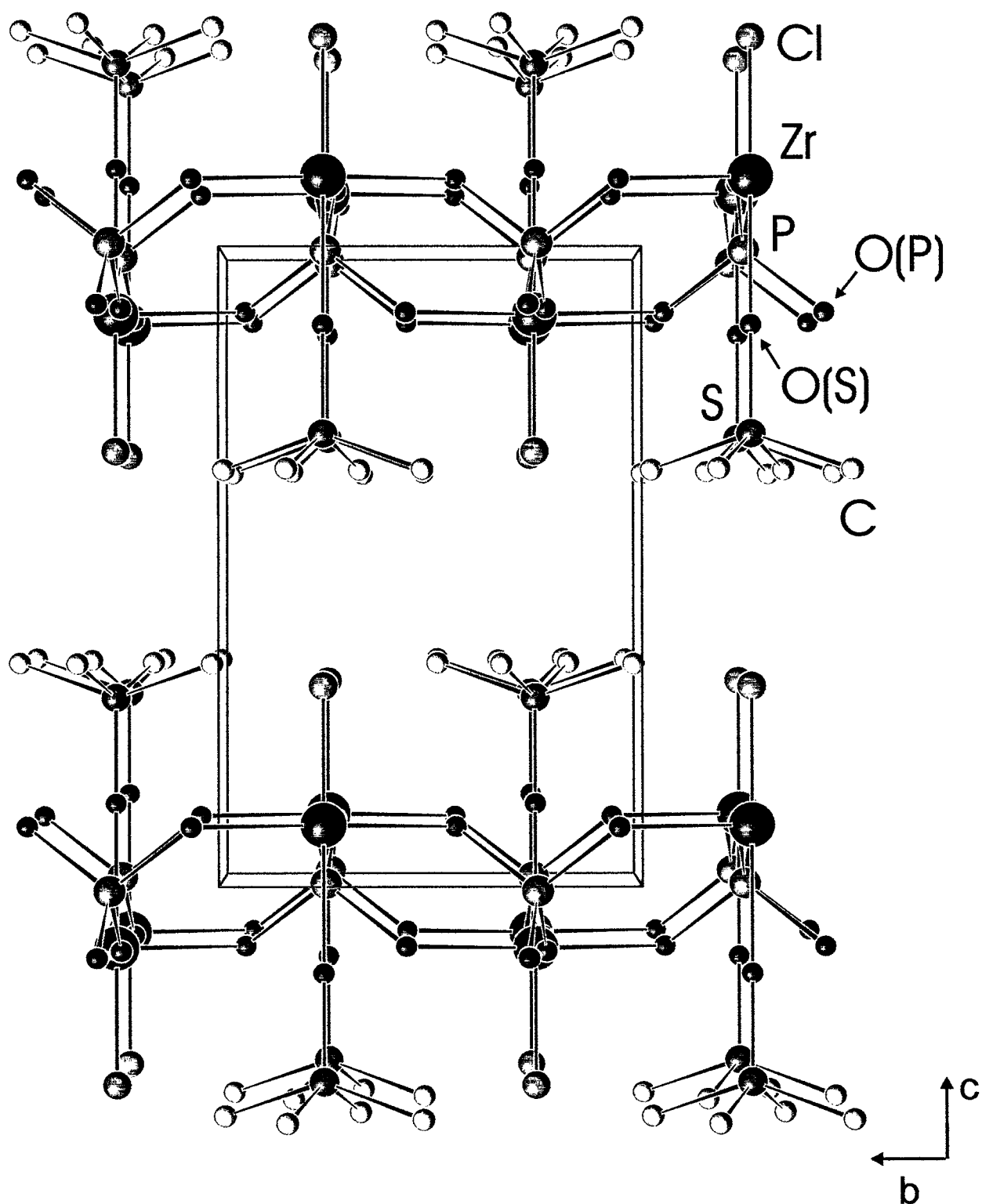Figure S2: Projection of the structure of $ZrPO_4Cl(CH_3)_2SO$ down the a axis.