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Tetrapyridinium tetrasulfatozirconate(IV) monohydrate

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Key indicators

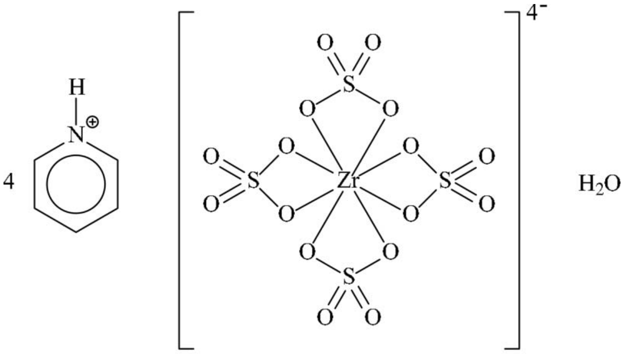
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.012 Å
R factor = 0.055
wR factor = 0.143
Data-to-parameter ratio = 16.7

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

The zirconium(IV) ion in the title compound, $(C_5H_6N)_4[Zr(SO_4)_4]\cdot H_2O$, exists in a distorted dodecahedral geometry with four bidentate sulfate groups. The tetraanion, two of the pyridinium cations and water molecule all lie on special positions with *m* site symmetry. A network of N—H···O and O—H···O hydrogen bonds helps to stabilize the structure.

Comment

The inorganic zirconium sulfates $Zr(OH)_2(SO_4)\cdot 3H_2O$ (Gascoigne *et al.*, 1994), $Zr(OH)_2(SO_4)\cdot H_2O$ (Hansson, 1973), Zr(OH)2(SO4) (El Brahimi *et al.*, 1988) and $Zr_2(OH)_2(SO_4)_3\cdot 4H_2O$ (McWhan & Lundgren, 1966) are some of the intermediate phases that are probably formed in the precipitation of zirconium hydroxide sulfates (Bochkarev *et al.*, 1966; Nekhamkin *et al.*, 1981). Some double salts have also been crystallographically authenticated, for example, $K_3Zr(OH)(SO_4)_3\cdot 2H_2O$ (Kuznetsov *et al.*, 1991), $K_2Zr(SO_4)_3\cdot 2H_2O$ (Mumme, 1971; Porai-Koshits *et al.*, 1972) and $Na_2Zr(SO_4)_3\cdot 2H_2O$ (Bear & Mumme, 1971). The other metal salt used in the synthesis of such double salts can be replaced by an amine that can also serve as a base; the resulting protonated ammonium cations would not bind directly to the Zr atom.



(I)

The $[Zr(SO_4)_4]^{4-}$ anion in the title compound, (I) (Fig. 1), contains four sulfate groups whose chelation to the Zr atom results in a ZrO_8 dodecahedron (Fig. 2); chelation by four sulfate groups is unprecedented in the structural literature of zirconium sulfates. In the various other modifications of zirconium sulfate, the metal atom is only seven-coordinate (Bear & Mumme, 1970). The charge of the resulting anion is balanced by four pyridinium cations (Fig. 1) and a water molecule of hydration is also present.

Atoms Zr1, S1, S2, O1, O2, O4 and O5 of the tetraanion, an N and a C atom of two of the three symmetry-independent

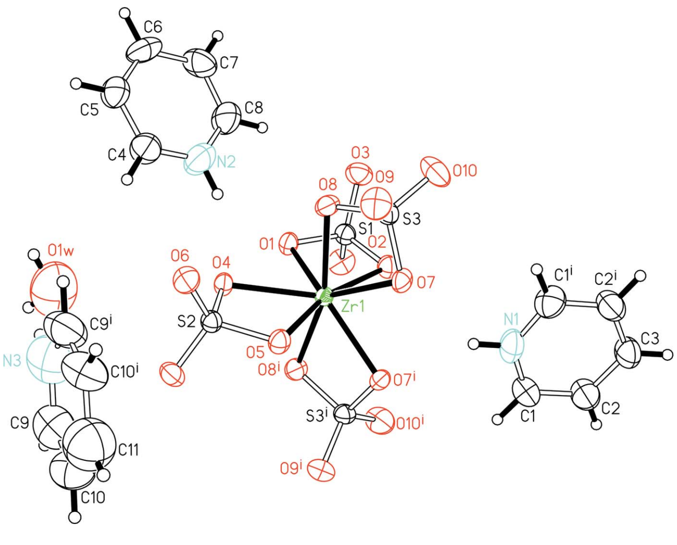


Figure 1
View of (I), showing 30% displacement ellipsoids (arbitrary spheres for the H atoms). [Symmetry code: (i) $1 - x, y, z$.]

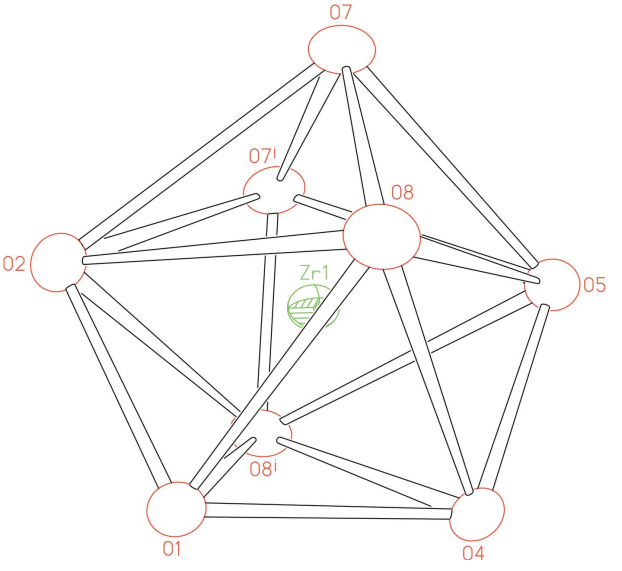


Figure 2
Detail of (I), illustrating the dodecahedral coordination of the Zr atom.

cations and the water molecule O atom all lie on special positions with *m* site symmetry. The cations, tetraanion and water molecule interact by way of N—H···O and O—H···O hydrogen bonds (Table 2), giving rise to a three-dimensional network.

Experimental

Zironium oxychloride octahydrate (0.32 g, 1 mmol) and sulfuric acid (98%, 0.5 ml, 9 mmol) were dissolved in water (2 ml). Pyridine (1.2 ml, 14 mmol) was added to give a pH of about 5. Colorless crystals of (I) separated from the solution in about 80% yield after two weeks.

Crystal data

$(C_5H_6N)_4[Zr(SO_4)_4]\cdot H_2O$
$M_r = 813.91$
Orthorhombic, $Cmc2_1$
$a = 11.355$ (1) Å
$b = 17.568$ (2) Å
$c = 16.102$ (2) Å
$V = 3212.2$ (6) Å^3
$Z = 4$
$D_x = 1.683$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1681 reflections
$\theta = 2.3$–$21.2°$
$\mu = 0.68$ mm^{-1}
$T = 295$ (2) K
Block, colorless
0.17 × 0.12 × 0.07 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.768$, $T_{max} = 0.955$
9733 measured reflections

3766 independent reflections
2961 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 12$
$k = -22 \rightarrow 21$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.143$
$S = 1.01$
3766 reflections
226 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0816P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.80$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}
Absolute structure: Flack (1983) 1783 Friedel pairs
Flack parameter: −0.04 (8)

Table 1
Selected geometric parameters (Å, °).

Zr1—O1	2.189 (6)	Zr1—O5	2.211 (6)
Zr1—O2	2.183 (6)	Zr1—O7	2.191 (4)
Zr1—O4	2.220 (5)	Zr1—O8	2.180 (4)
O1—Zr1—O2	63.8 (2)	O4—Zr1—O5	62.7 (2)
O1—Zr1—O4	69.7 (2)	O4—Zr1—O7	130.3 (2)
O1—Zr1—O5	132.4 (2)	O4—Zr1—O8	82.6 (1)
O1—Zr1—O7	132.4 (2)	O5—Zr1—O7	82.5 (2)
O1—Zr1—O8	82.0 (1)	O5—Zr1—O8	91.7 (1)
O2—Zr1—O4	133.6 (2)	O7—Zr1—O7^i	72.6 (2)
O2—Zr1—O5	163.7 (2)	O7—Zr1—O8	63.1 (2)
O2—Zr1—O7	84.4 (2)	O7—Zr1—O8^i	135.7 (2)
O2—Zr1—O8	90.9 (1)		

Symmetry code: (i) $-x + 1, y, z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1w—H1w···O10^{ii}	0.85	1.83	2.656 (9)	162
N1—H1n···O7	0.86	2.23	2.965 (9)	143
N1—H1n···O7^i	0.86	2.23	2.965 (9)	143
N2—H2n···O4	0.86	1.99	2.801 (9)	157
N3—H3n···O1w	0.86	1.75	2.56 (2)	156

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

The three pyridinium cations, two of which are generated by mirror symmetry, showed excessive thermal motion. This necessitated restraining the C—N distances to 1.350 (5) Å and the C—C distances to 1.390 (5) Å. The pyridine rings were also restrained to be nearly planar and the vibration of their atoms to be nearly isotropic. The carbon- and nitrogen-bound H atoms were positioned geometrically [C—H = 0.93 Å and N—H = 0.86 Å; $U_{iso}(H) = 1.2U_{eq}(C,N)$] and they were included in the refinement in the riding-model approximation. The water H atom was placed in a chemically sensible position on the basis of hydrogen bonding but its position was not refined [$U_{iso}(H) =$

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$1.2U_{eq}(O)$]. The distance between the water and pyridinium H atoms exceeds 2.0 Å.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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