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Pentakis(ethane-1,2-diammonium) aquapentasulfato-$\kappa^3O;\kappa^4O,O'$-zirconate(IV) diaquatetrasulfato-$\kappa^2O;\kappa^4O,O'$-zirconate(IV)

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The two independent Zr atoms in the asymmetric unit of the title structure, $(C_2H_{10}N_2)_5[Zr(SO_4)_5(H_2O)][Zr(SO_4)_4(H_2O)_2]$, are both eight-coordinate. In the docedahedral aquapentasulfatozirconate(IV) hexaanion, three of the sulfate groups are monodentate, whereas the other two chelate to the metal atom. In the square-antiprismatic diaquatetrasulfatozirconate(IV) tetraanion, two of the sulfate groups are monodentate and two are bidentate. Two of the five 1,2-ethanediammonium cations lie about crystallographic centres of inversion. The cations and anions are linked into a three-dimensional network architecture by hydrogen bonds.

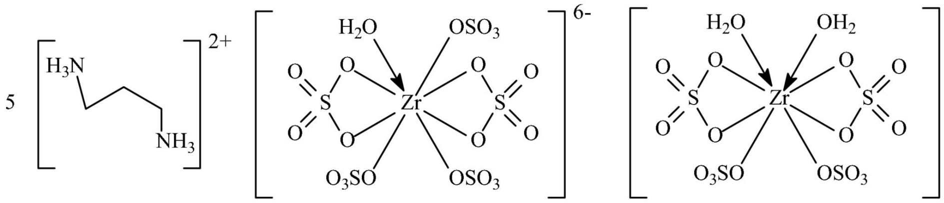
Key indicators

Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.010 Å
Disorder in solvent or counterion
R factor = 0.066
wR factor = 0.177
Data-to-parameter ratio = 12.1

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

Comment

A recent study reports the structure of propane-1,3-diammonium triaquatris(sulfato)zirconate(IV), in which a Zr atom is chelated by two of the three sulfate groups. The Zr atom is in a square-antiprismatic coordination geometry (Xu *et al.*, 2006). Using propane-1,3-diamine instead of ethylenediamine and following a similar synthetic procedure yields the title compound, (I), which has a different composition.


(I)

The asymmetric unit of (I) and symmetry-complete cations are shown in Fig. 1. There are five cations in the formula unit; the ten positive charges are balanced by a $[Zr(SO_4)_5(H_2O)]^{6-}$ hexaanion and a $[Zr(SO_4)_4(H_2O)_2]^{4-}$ tetraanion. In the hexaanion, two of the sulfate groups are chelating and the other three are monodentate, and these seven O atoms, in addition to a coordinated water molecule, give rise to a dodecahedral geometry at the metal centre (Fig. 2). On the other hand, in the tetraanion, two sulfate groups are chelating and two are monodentate; the square-antiprismatic geometry is completed by two water molecules (Fig. 3). Two of the five 1,2-ethanediammonium cations lie about crystallographic centres of inversion.

The cations and anions interact through hydrogen bonds (Table 2), resulting in a three-dimensional hydrogen-bonded network structure.

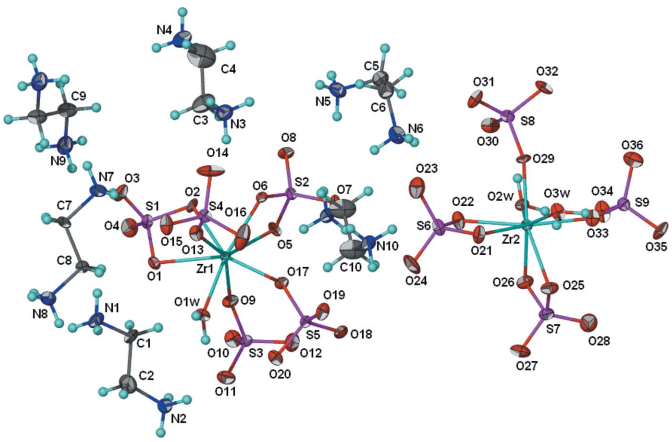


Figure 1
The asymmtric unit of (I) and the symmetry-complete cations. Displacement ellipsoids are drawn at the 50% probability level and H atoms as spheres of arbitrary radii. Only one disorder component is shown. Unlabelled atoms in the cations containing C9 and C10 are related by the symmetry operators $(1 - x, 1 - y, 2 - z)$ and $(-x, 1 - y, 1 - z)$, respectively.

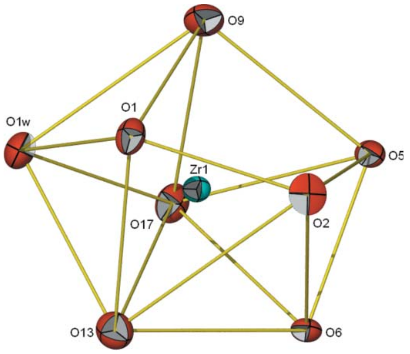


Figure 2
Representation of the dodecahedral geometry of Zr1 in the $[Zr(SO_4)_5(H_2O)]^{6-}$ anion.

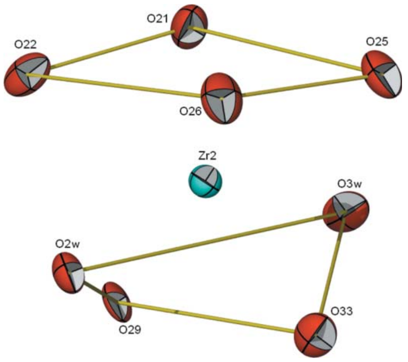


Figure 3
Representation of the square-antiprismatic geometry of Zr2 in the $[Zr(SO_4)_4(H_2O)_2]^{4-}$ anion.

Experimental

Zironium(IV) oxydichloride octahydrate (0.322 g, 1 mmol) was dissolved in water (10 ml). Sulfuric acid (98%) (0.50 ml, 8.33 mmol) and ethylenediamine (0.06 ml, 1 mmol) were added. The clear solution was set aside for a week for the formation of colourless block-shaped crystals of (I) (in 50% yield based on Zr).

Crystal data

$(C_2H_{10}N_2)_5[Zr(SO_4)_5(H_2O)]$-$[Zr(SO_4)_4(H_2O)_2]$
$M_r = 1411.63$
Monoclinic, $P2_1/c$
$a = 14.660$ (1) Å
$b = 16.845$ (1) Å
$c = 17.887$ (1) Å
$\beta = 93.298$ (2)°
$V = 4410.0$ (6) Å^3
$Z = 4$
$D_x = 2.126$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.03$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.09 × 0.07 × 0.05 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.913$, $T_{max} = 0.950$
23065 measured reflections
7733 independent reflections
4468 reflections with $I > 2\sigma(I)$
$R_{int} = 0.119$
$\theta_{max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.177$
$S = 0.99$
7733 reflections
637 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0719P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -0.76$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zr1—O1	2.287 (6)	Zr2—O21	2.180 (6)
Zr1—O2	2.248 (6)	Zr2—O22	2.216 (6)
Zr1—O5	2.296 (6)	Zr2—O25	2.260 (7)
Zr1—O6	2.245 (6)	Zr2—O26	2.212 (7)
Zr1—O9	2.096 (6)	Zr2—O29	2.094 (6)
Zr1—O13	2.115 (6)	Zr2—O33	2.112 (6)
Zr1—O17	2.100 (6)	Zr2—O2*W*	2.213 (6)
Zr1—O1*W*	2.235 (6)	Zr2—O3*W*	2.289 (6)
O1—Zr1—O2	60.5 (2)	O21—Zr2—O22	62.0 (2)
O1—Zr1—O5	124.5 (2)	O21—Zr2—O25	80.4 (2)
O1—Zr1—O6	128.3 (2)	O21—Zr2—O26	107.2 (3)
O1—Zr1—O9	82.1 (2)	O21—Zr2—O29	91.0 (3)
O1—Zr1—O13	76.9 (2)	O21—Zr2—O33	145.8 (2)
O1—Zr1—O17	148.6 (2)	O21—Zr2—O2*W*	132.5 (2)
O1—Zr1—O1*W*	72.3 (2)	O21—Zr2—O3*W*	71.7 (2)
O2—Zr1—O5	73.2 (2)	O22—Zr2—O25	117.3 (2)
O2—Zr1—O6	77.9 (2)	O22—Zr2—O26	83.0 (2)
O2—Zr1—O9	96.6 (2)	O22—Zr2—O29	85.3 (2)
O2—Zr1—O13	90.1 (2)	O22—Zr2—O33	151.6 (2)
O2—Zr1—O17	150.5 (2)	O22—Zr2—O2*W*	70.9 (2)
O2—Zr1—O1*W*	132.7 (2)	O22—Zr2—O3*W*	128.8 (2)
O5—Zr1—O6	61.4 (2)	O25—Zr2—O26	61.5 (2)
O5—Zr1—O9	74.2 (2)	O25—Zr2—O29	146.8 (2)
O5—Zr1—O13	134.4 (2)	O25—Zr2—O33	81.9 (2)
O5—Zr1—O17	79.8 (2)	O25—Zr2—O2*W*	129.0 (2)
O5—Zr1—O1*W*	145.2 (2)	O25—Zr2—O3*W*	72.2 (2)
O6—Zr1—O9	135.0 (2)	O26—Zr2—O29	150.3 (2)
O6—Zr1—O13	73.8 (2)	O26—Zr2—O33	89.4 (3)
O6—Zr1—O17	79.0 (2)	O26—Zr2—O2*W*	70.6 (2)
O6—Zr1—O1*W*	136.4 (2)	O26—Zr2—O3*W*	132.9 (2)
O9—Zr1—O13	151.1 (3)	O29—Zr2—O33	88.0 (3)
O9—Zr1—O1*W*	79.2 (2)	O29—Zr2—O2*W*	79.8 (2)
O9—Zr1—O17	87.0 (2)	O29—Zr2—O3*W*	74.6 (2)
O13—Zr1—O17	100.8 (2)	O33—Zr2—O2*W*	80.8 (2)
O13—Zr1—O1*W*	75.8 (2)	O33—Zr2—O3*W*	75.1 (2)
O17—Zr1—O1*W*	76.8 (2)	O2*W*—Zr2—O3*W*	145.2 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*1···O11$^{\rm i}$	0.85	2.16	2.921 (9)	148
O1*W*—H1*W*2···O20	0.85	1.90	2.678 (9)	150
O2*W*—H2*W*1···O30	0.84	1.92	2.708 (9)	156
O2*W*—H2*W*2···O34	0.85	1.83	2.630 (9)	156
O3*W*—H3*W*1···O4$^{\rm ii}$	0.86	2.02	2.814 (9)	154
O3*W*—H3*W*2···O15$^{\rm iii}$	0.86	2.00	2.715 (8)	140
N1—H1*A*···O4	0.85	2.32	3.10 (1)	154
N1—H1*B*···O20$^{\rm i}$	0.85	1.98	2.83 (1)	175
N1—H1*C*···O28$^{\rm iv}$	0.85	2.10	2.93 (1)	166
N2—H2*A*···O16$^{\rm i}$	0.85	2.28	2.93 (1)	134
N2—H2*B*···O11	0.85	2.05	2.87 (1)	163
N2—H2*C*···O31$^{\rm v}$	0.85	2.20	3.00 (1)	156
N3—H3*A*···O14	0.85	2.18	2.73 (1)	123
N3—H3*B*···O30$^{\rm vi}$	0.85	2.09	2.93 (1)	168
N3—H3*C*···O26$^{\rm vii}$	0.85	2.42	3.08 (1)	135
N3—H3*C*···O27$^{\rm vii}$	0.85	2.49	3.21 (1)	142
N4—H4*A*···O7$^{\rm vii}$	0.85	2.12	2.86 (1)	146
N4—H4*B*···O36$^{\rm vi}$	0.85	2.43	3.01 (1)	126
N4—H4*C*···O18$^{\rm vii}$	0.85	2.05	2.85 (1)	156
N5—H5*A*···O19$^{\rm vii}$	0.85	2.09	2.90 (1)	161
N5—H5*B*···O24$^{\rm vii}$	0.85	2.38	2.93 (1)	123
N5—H5*C*···O8	0.85	2.45	2.86 (1)	110
N5—H5*C*···O35$^{\rm viii}$	0.85	2.43	3.15 (1)	142
N5—H5*C*···O34$^{\rm viii}$	0.85	2.44	3.21 (1)	151
N5—H5*C*···O8	0.85	2.45	2.86 (1)	110
N6—H6*A*···O23	0.85	2.17	2.88 (1)	140
N6—H6*B*···O30	0.85	2.45	3.02 (1)	125
N6—H6*C*···O7	0.85	2.08	2.89 (1)	158
N7—H7*A*···O32$^{\rm vi}$	0.85	2.31	2.90 (1)	127
N7—H7*A*···O10$^{\rm ix}$	0.85	2.43	3.13 (1)	141
N7—H7*B*···O3	0.85	2.13	2.92 (1)	153
N7—H7*C*···O15	0.85	2.06	2.82 (1)	148
N8—H8*A*···O18$^{\rm i}$	0.85	2.18	2.84 (1)	135
N8—H8*B*···O35$^{\rm iv}$	0.85	2.11	2.89 (1)	152
N8—H8*C*···O2$^{\rm ix}$	0.85	2.15	2.99 (1)	169
N9—H9*A*···O10$^{\rm vii}$	0.85	2.18	2.84 (1)	135
N9—H9*B*···O32$^{\rm iv}$	0.85	2.02	2.81 (1)	154
N9—H9*C*···O3	0.85	2.25	2.95 (1)	140
N10—H10*A*···O27$^{\rm vii}$	0.85	2.41	3.25 (1)	168
N10—H10*B*···O16	0.85	2.13	2.89 (1)	148
N10—H10*C*···O24	0.85	2.53	3.37 (1)	167

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x, -y+1, -z+1$; (iv) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$; (v) $x+1, y, z$; (vi) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; (vii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (viii) $-x, -y, -z+1$; (ix) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.

The ammonium and carbon-bound H atoms were treated as riding, with N—H = 0.85 Å and C—H = 0.97 Å, and were included in the refinement with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm N,C})$. The water H atoms were placed in chemically sensible positions on the basis of hydrogen bonds but they were not refined; their displacement parameters were similarly tied. One of the cations is disordered over two sites; the occupancies of the major and minor components were arbitrarily fixed at 0.5. For all cations, the C—N distances were restrained to 1.450 (5) Å and the C—C distances to 1.500 (5) Å. The anisotropic dispacement parameters of the C, N and O atoms were restrained to be nearly isotropic.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2006).

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