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Key indicators

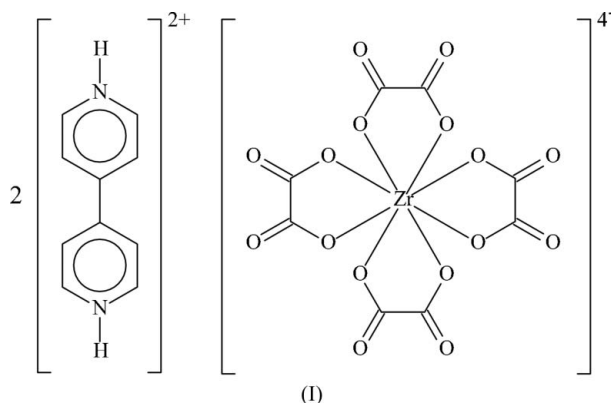
Single-crystal X-ray study
 $T = 295\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
 R factor = 0.047
 wR factor = 0.112
Data-to-parameter ratio = 13.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis(4,4'-bipyridinium) tetrakis(oxalato- $\kappa^2\text{O},\text{O}'$)-
zirconate(IV)The Zr atom in the title salt, $(\text{C}_{10}\text{H}_{10}\text{N}_2)_2[\text{Zr}(\text{C}_2\text{O}_4)_4]$, is chelated by four oxalate anions in a square-antiprismatic geometry. The cations and anions are linked by short $\text{N}-\text{H}\cdots\text{O}$ and long $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds into a layer structure. The Zr atom lies on a special position of site symmetry 2.

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Comment

The oxalate dianion is a common species used to chelate to transition metals; with the first-row transition metals, the packing of four such chelating groups around the metal atom is rarely encountered owing to the small size of the metal atom. Few examples of discrete tetraoxalatometallates have been reported, and the hydrated sodium (Glen *et al.*, 1963) and potassium (Kojic-Prodic *et al.*, 1978) tetraoxalatozirconates constitute rare examples. This study continues with an earlier report on *N*-methylpiperadinium(2+) trisoxalatozirconate(IV); the anion exists as a polyanionic chain in which one oxalate simultaneously chelates to two zirconium atoms (Fu *et al.*, 2005). Tetrakis(4,4'-bipyridinium) tetrakisoxalatozirconate(IV), (I), consists of discrete cations and anions (Fig. 1). The crystal structure features short $\text{N}-\text{H}\cdots\text{O}$ and long $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds (Fig. 2). The short hydrogen bonds link the ions into a layer structure, the long ones further consolidating the ions within the layers (Table 2). In the tetraanion, the Zr atom, lying on a special position of site symmetry 2, shows square-antiprismatic coordination (Fig. 3).

Experimental

Zirconium(IV) oxychloride (0.32 g, 1 mmol), oxalic acid dihydrate (0.50 g, 4 mmol) and 4,4'-bipyridine (0.19 g, 1 mmol) were dissolved in water (10 ml). The solution was set aside for a day for crystals of the salt to deposit from solution. The salt was isolated in about 30% yield.

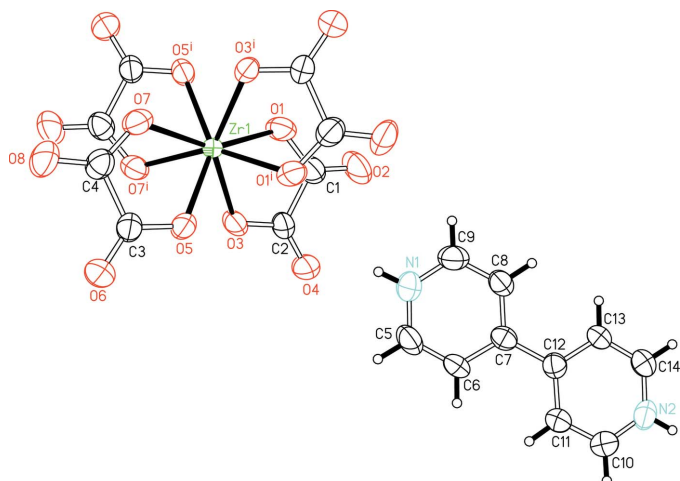


Figure 1
ORTEP (Johnson, 1976) plot, illustrating the coordination geometry of the Zr atom in (I). Displacement ellipsoids are drawn at the 70% probability level and H atoms are drawn as spheres of arbitrary radii. [Symmetry code: (i) $1 - x, 1 + y, \frac{1}{2} - z$.]

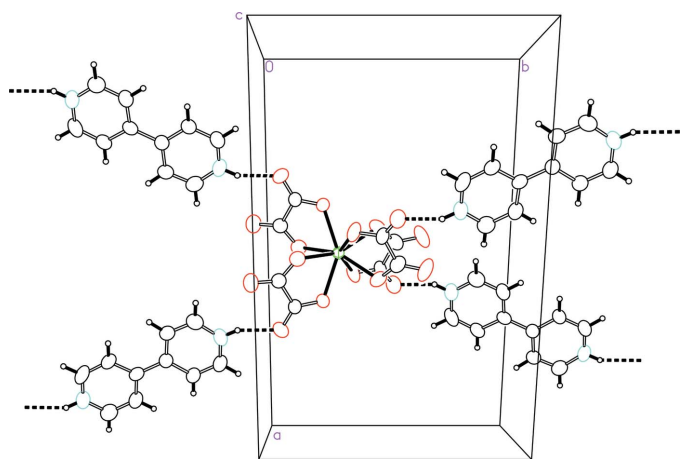


Figure 2
ORTEP (Johnson, 1976) plot of the layer structure formed by strong and weak hydrogen bonds (dashed lines).

Crystal data

(C₁₀H₁₀N₂)₂[Zr(C₂O₄)₄]
M_r = 759.70
 Monoclinic, C2/c
a = 19.447 (2) Å
b = 10.986 (1) Å
c = 15.084 (2) Å
 β = 121.231 (2)°
V = 2755.6 (5) Å³
Z = 4

D_x = 1.831 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 1612 reflections
 θ = 2.2–23.1°
 μ = 0.49 mm⁻¹
T = 295 (2) K
 Plate, colorless
 0.18 × 0.16 × 0.07 mm

Data collection

Bruker APEX area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.470, *T_{max}* = 0.966
 7967 measured reflections

3097 independent reflections
 2340 reflections with *I* > 2σ(*I*)
R_{int} = 0.045
 θ_{max} = 27.5°
h = -25 → 13
k = -14 → 12
l = -19 → 19

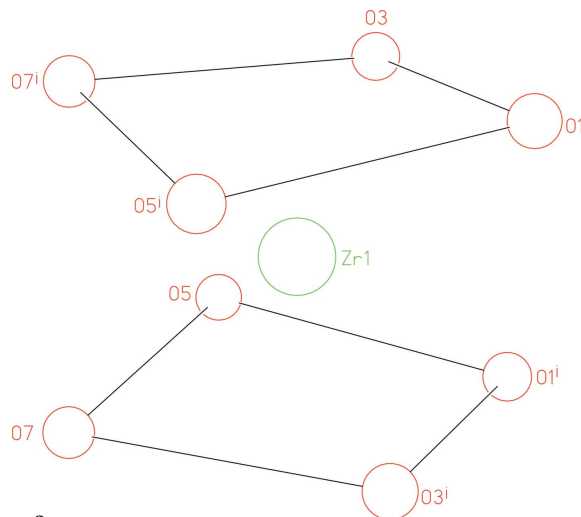


Figure 3
The square-antiprismatic coordination of the Zr atom in the tetraanion (symmetry code as in Fig. 1 and Table 1).

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.047
wR (*F*²) = 0.112
S = 1.03
 3097 reflections
 230 parameters
 H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0564*P*)² + 0.727*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.65 e Å⁻³
 Δρ_{min} = -0.60 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Zr1—O1	2.201 (2)	Zr1—O5	2.197 (2)
Zr1—O3	2.189 (2)	Zr1—O7	2.223 (2)
O1—Zr1—O1 ⁱ	76.9 (1)	O3—Zr1—O5	71.4 (1)
O1—Zr1—O3	70.7 (1)	O3—Zr1—O5 ⁱ	120.3 (1)
O1—Zr1—O3 ⁱ	81.9 (1)	O3—Zr1—O7	135.2 (1)
O1—Zr1—O5	136.0 (1)	O3—Zr1—O7 ⁱ	76.5 (1)
O1—Zr1—O5 ⁱ	76.4 (1)	O5—Zr1—O5 ⁱ	144.0 (1)
O1—Zr1—O7	152.8 (1)	O5—Zr1—O7	70.4 (1)
O1—Zr1—O7 ⁱ	110.6 (1)	O5—Zr1—O7 ⁱ	81.1 (1)
O3—Zr1—O3 ⁱ	144.9 (1)	O7—Zr1—O7 ⁱ	75.3 (1)

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

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O4	0.85 (1)	1.86 (2)	2.658 (4)	155 (4)
N2—H2...O6 ⁱⁱⁱ	0.86 (1)	1.89 (2)	2.683 (4)	154 (4)
C5—H5...O6 ⁱⁱⁱ	0.93	2.27	3.152 (5)	159
C6—H6...O5 ⁱⁱⁱ	0.93	2.47	3.199 (4)	135
C8—H8...O7 ^{iv}	0.93	2.35	3.193 (4)	150
C9—H9...O8 ^{iv}	0.93	2.25	3.078 (4)	148
C10—H10...O2 ^v	0.93	2.29	3.085 (5)	144
C11—H11...O1 ^v	0.93	2.34	3.179 (4)	150
C13—H13...O3 ^{vi}	0.93	2.46	3.163 (4)	133
C14—H14...O4 ^{vi}	0.93	2.29	3.184 (4)	160

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

The carbon-bound H atoms were placed at calculated positions [$C-H = 0.93 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$] and were included in the refinement in the riding-model approximation. The nitrogen-bound H atoms were located in a difference Fourier map, and were refined with an $N-H = 0.85(1) \text{ \AA}$ distance restraint. Their displacement parameters were freely refined.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; 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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