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catena-Poly[*N*-methylpiperazinium(2+) [[bis(oxalato-$\kappa^2 O,O'$)zirconate(IV)]-μ_2-oxalato-$\kappa^4 O,O':O'',O'''$]]

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Key indicators

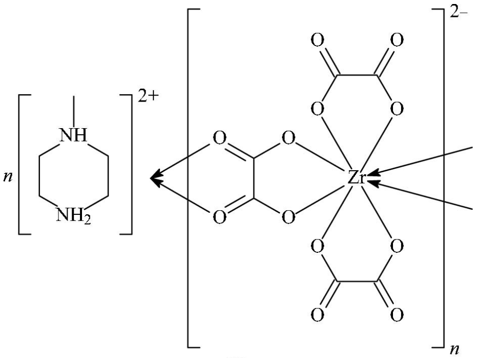
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.002 Å
R factor = 0.019
wR factor = 0.054
Data-to-parameter ratio = 13.3

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

The Zr atom in the title compound, $\{(C_5H_{11}N_2)[Zr(C_2O_4)_3]\}_n$, is chelated by four oxalate groups in a square-antiprismatic geometry. Bridging by one of the three oxalate groups in the asymmetric unit gives rises to a helical tris(oxalato)zirconate chain that propagates along the b axis of the unit cell. The dications surround the chains and are tightly hydrogen bonded to them, resulting in a three-dimensional network.

Comment

In common with other metals, zirconium oxalate complexes can serve as precursors in the preparation of ternary oxides; among these are some species having four oxalate groups attached to the Zr atom, for example, $Na_4[Zr(C_2O_4)_4]\cdot 3H_2O$ (Glen *et al.*, 1963), $K_4[Zr(C_2O_4)_4]\cdot .5H_2O$ (Kojić-Prodić *et al.*, 1978), $Ba_2[Zr(C_2O_4)_4]\cdot 3H_2O$ (Vertruyen *et al.*, 2004) and $Pb_2[Zr(C_2O_4)_4]\cdot nH_2O$ (Boudaren *et al.*, 2000). The ammonium salt formulated as $(NH_4)_2[CdZr(C_2O_4)_4]\cdot 4H_2O$ has distinct $[Zr(C_2O_4)_4]^{4-}$ and $[Cd(C_2O_4)_4]^{6-}$ anions. The use of an amine has extended the scope of such syntheses as the resulting ammonium complexes, when thermolysed, readily furnish the mixed metal oxides, as exemplified by $(NH_3CH_2CH_2NH_3)[CdZr(C_2O_4)_4]\cdot 4H_2O$ (Jeanneau *et al.*, 2002). Our interest in oxalatozirconates comes from our observations that ammonium counter-ions exert an influence on the oxalatozirconate anion, which can exist as discrete anions or as polyanionic chains depending on the nature of the amine used in the hydrothermal reaction (Fu *et al.*, 2002).



(I)

The bis-piperazinium(2+) salt, $(C_4H_{12}N_2)_2[Zr(C_2O_4)_4]$, which arises from a hydrothermal reaction involving zirconyl chloride, oxalic acid and piperizine (Fu *et al.*, 2005), has four oxalate groups chelating the metal atom in a nearly isobidentate manner. It can also be synthesized without the use of hydrothermal conditions (Sun *et al.*, 2004). Using *N*-methylpiperizine as the templating reagent in an analogous hydrothermal synthesis, the title compound, (I), is obtained. The

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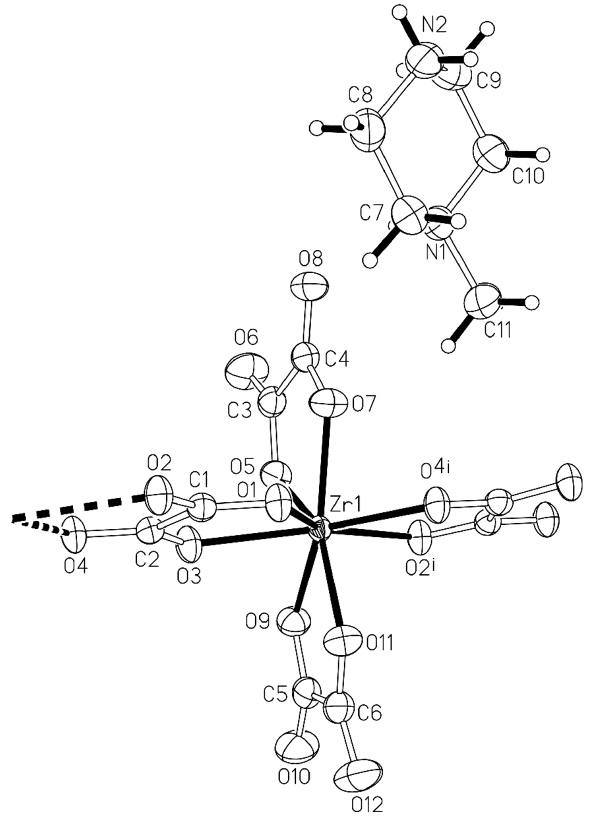

Figure 1
View of a fragment of (I). Displacement ellipsoids are drawn at the 70% probability level and H atoms are drawn as spheres of arbitrary radius. [Symmetry code: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

zirconate dianion has three crystallographically distinct chelating oxalate groups, but one of them also functions as a bridging unit to afford a polyanionic tris(oxalato)zirconate chain that is surrounded by *N*-methylpiperizinium(2+) cations (Fig. 1 and Table 1).

The eight O atoms surrounding the metal atom comprise an approximate square antiprism (Fig. 2). Although the two square planes are buckled [r.m.s. deviation from the mean plane (Δ) for O1/O3/O9/O11 = 0.30 Å; Δ for O2^i/O4^i/O5/O7 = 0.11 Å, see Table 1 for symmetry code], the planes are almost parallel to each other [dihedral angle = 1.4 (1)°]. Bridging by one of the three oxalate groups leads to the formation of a helical chain that runs along the *b* axis of the unit cell (Fig. 3). The cations surrounding the chains are held in place by hydrogen bonds (Table 2); the manner of linkage leads to a three-dimensional network structure.

The tris(oxalato)zirconate unit in the crystal structure of $K_2[Zr(C_2O_4)_3]\cdot C_2H_2O_4\cdot H_2O$ (Baggio *et al.*, 1997*a*) also has its Zr atom in an eight-coordinate environment made up of four chelating oxalate groups, and the bridging behavior of one of the three gives rise to the formation of a zigzag chain. The geometry at the metal atom is described as dodecahedral. In the crystal structure of $K_6[Zr(C_2O_4)_3][C_2O_4]$, the Zr atom is also in a dodecahedral environment, but the bridging nature of one of the oxalate groups gives rise instead to the formation of a dinuclear $[(C_2O_4)_7Zr_2]$ hexaanion (Baggio *et al.*, 1997*b*).

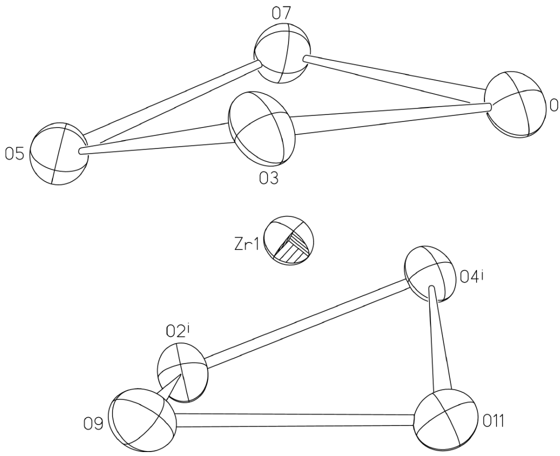

Figure 2
The square antiprismatic environment of the Zr^{IV} atom.

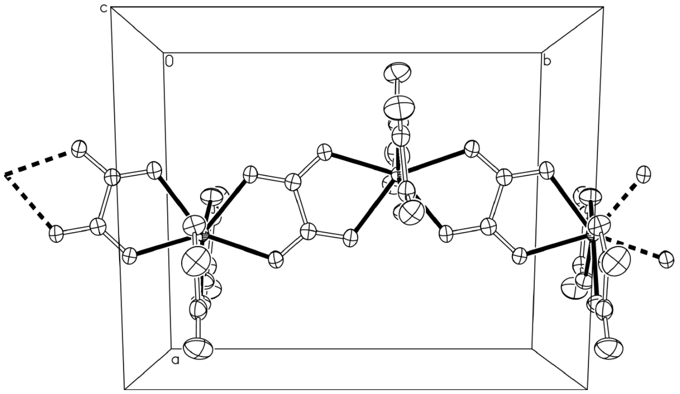

Figure 3
A view of the anionic chain in (I).

Experimental

Zirconium oxychloride octahydrate (0.32 g, 10 mmol) was dissolved in water (10 ml) along with oxalic acid dihydrate (0.50 g, 4 mol). The addition of *N*-methylpiperazine (0.10 g, 10 mmol) led to the formation of a white solid. The suspension was placed in an autoclave and was heated at 383 K for 2 d. Colorless crystals of (I) were isolated when the bomb was cooled slowly. Found (calculated) for $C_{11}H_{14}N_2O_{11}Zr$ (%): C 28.91 (28.88), H 3.02 (3.08), N 6.14 (6.13).

Crystal data

$(C_5H_{11}N_2)[Zr(C_2O_4)_3]$
$M_r = 457.46$
Monoclinic, $P2_1/c$
$a = 9.5936$ (5) Å
$b = 11.3569$ (5) Å
$c = 13.9792$ (7) Å
$\beta = 108.023$ (1)°
$V = 1448.4$ (1) Å^3
$Z = 4$

$D_x = 2.098$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 5754 reflections
$\theta = 2.4$–28.5°
$\mu = 0.84$ mm^{-1}
$T = 295$ (2) K
Prism, colorless
0.38 × 0.29 × 0.20 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.712$, $T_{max} = 0.850$
15328 measured reflections

3273 independent reflections
3114 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -18 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.054$
$S = 1.06$
3273 reflections
247 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 0.4993P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.54$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zr1—O1	2.318 (1)	Zr1—O5	2.165 (1)
Zr1—O2^{i}	2.260 (1)	Zr1—O7	2.132 (1)
Zr1—O3	2.222 (1)	Zr1—O9	2.190 (1)
Zr1—O4^{i}	2.263 (1)	Zr1—O11	2.124 (1)

O1—Zr1—O2^{i}	145.59 (3)	O3—Zr1—O5	76.15 (3)
O1—Zr1—O3	70.63 (3)	O3—Zr1—O7	100.27 (4)
O1—Zr1—O4^{i}	75.13 (4)	O3—Zr1—O9	75.85 (3)
O1—Zr1—O5	126.76 (3)	O3—Zr1—O11	92.30 (4)
O1—Zr1—O7	74.66 (4)	O4^{i}—Zr1—O5	129.76 (3)
O1—Zr1—O9	132.70 (3)	O4^{i}—Zr1—O7	73.39 (4)
O1—Zr1—O11	76.18 (4)	O4^{i}—Zr1—O9	128.49 (3)
O2^{i}—Zr1—O3	143.72 (4)	O4^{i}—Zr1—O11	76.12 (4)
O2^{i}—Zr1—O4^{i}	70.46 (3)	O5—Zr1—O7	71.76 (4)
O2^{i}—Zr1—O5	77.67 (3)	O5—Zr1—O9	73.52 (4)
O2^{i}—Zr1—O7	94.87 (4)	O5—Zr1—O11	146.14 (4)
O2^{i}—Zr1—O9	72.92 (3)	O7—Zr1—O9	144.93 (4)
O2^{i}—Zr1—O11	95.67 (4)	O7—Zr1—O11	142.09 (4)
O3—Zr1—O4^{i}	145.59 (3)	O9—Zr1—O11	72.80 (4)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H11$\cdots$O8	0.85 (1)	2.11 (1)	2.892 (2)	153 (2)
N2—H21$\cdots$O2^{ii}	0.86 (1)	2.27 (2)	2.948 (2)	136 (2)
N2—H21$\cdots$O5^{iii}	0.86 (1)	2.19 (2)	2.879 (2)	137 (2)
N2—H22$\cdots$O10^{iv}	0.86 (1)	1.99 (1)	2.780 (2)	153 (2)
N2—H22$\cdots$O12^{iv}	0.86 (1)	2.46 (2)	3.052 (2)	127 (2)

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

The carbon-bound H atoms were placed at calculated positions (C—H = 0.97 Å for the methylene H atoms and C—H = 0.98 Å for the methyl H atoms) and were included in the refinement in the riding-model approximation, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for the methylene H atoms and 1.5$U_{\rm eq}$(C) for the methyl H atoms. The amino H atoms were located in difference maps and refined with a distance restraint of N—H = 0.85 (1) Å; their $U_{\rm iso}$ values were freely refined.

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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