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Tris(biacetyl dihydrazone-κ^2N,N')zinc(II) bis(perchlorate) at 110 K

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Key indicators

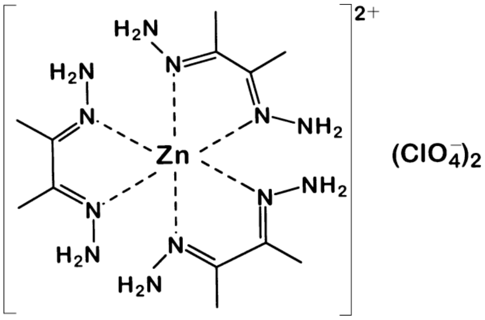
Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.004 Å
R factor = 0.035
wR factor = 0.090
Data-to-parameter ratio = 15.7

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

The crystal structure of the title compound, $[Zn(C_4H_{10}N_4)_3](ClO_4)_2$, has been precisely determined at *ca* 110 K. The organometallic cation, which is located on a $\overline{3}$ axis, is characterized by an approximate octahedral geometry, with each of the ligands occupying two coordination sites around the metal.

Comment

We have been exploring the coordination chemistry of a large series of polyimine ligands with transition metal ions (Patra & Goldberg, 2003*a*,*b*), as well as with metalloporphyrins (Diskin-Posner *et al.*, 2001). We describe here the structure of a 1:3 zinc complex with the simple bidentate biacetyl dihydrazone ligand; the analogous and isomorphous cadmium complex is reported in the following paper (Tirosh *et al.*, 2005).



(I)

The title compound, (I), crystallizes in the trigonal space group $P\overline{3}c1$ with two units of the $[Zn(C_4H_{10}N_4)_3]^{2+}$ cationic complex and four ClO_4^- anions in the unit cell. The Zn^{II} atom is located on a $\overline{3}$ axis, while the perchlorate anion is located on a threefold rotation axis. The cation is characterized by perfect $\overline{3}$ symmetry, in which three chelating ligands occupy the octahedral coordination sites of the zinc metal ion (Fig. 1). The imine N atoms of the ligand provide the coordination sites to the central metal ion. Selected geometric parameters are listed in Table 1.

The conformation about the central C—C bond of the ligand is *cis*, with the two C=N bonds being nearly coplanar, to direct the two imine coordinating sites towards the metal centre. The N—Zn—N bond angle involving two coordinating N atoms of a given ligand is 74.33 (11)°. In the free form of the ligand, the N—N=C—C=N—N backbone adopts a planar *anti* conformation (Hauer *et al.*, 1987). Compound (I) was found to be isostructural with the nickel(II) dinitrate complex of the same ligand, published previously. The latter exhibits, however, only approximate threefold symmetry, crystallizing

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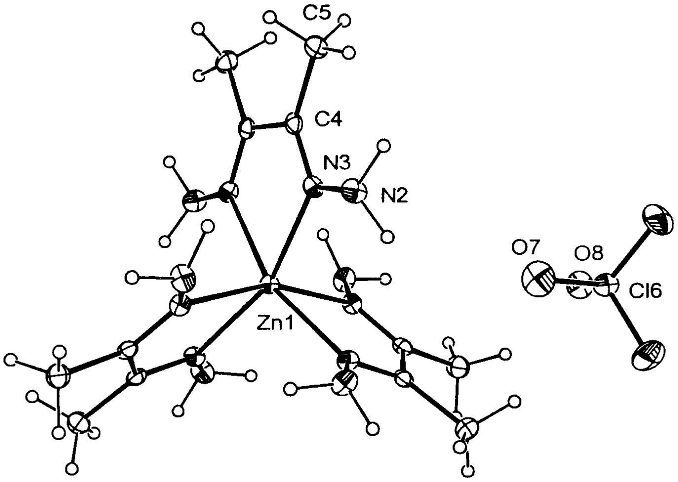

Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Atom Zn1 lies on a $\bar{3}$ axis and atoms Cl6 and O8 lie on a threefold rotation axis. One of the anions has been omitted for clarity.

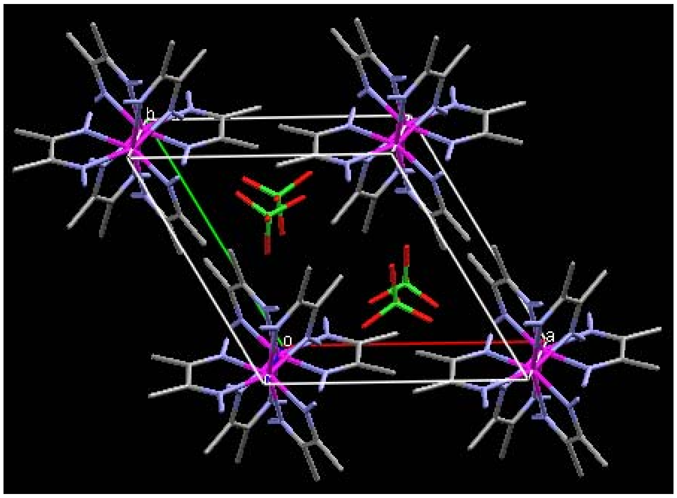

Figure 2
Crystal packing of (I), viewed approximately down the *c* axis.

in the monoclinic space group $P2_1/n$ with $Z = 4$ (Romanenko *et al.*, 1989). The crystal packing of (I) is shown in Fig. 2.

Experimental

Compound (I) was synthesized by reacting equimolar amounts of zinc acetate dihydrate, biacetyl dihydrazone and sodium perchlorate dissolved in hot methanol, followed by slow crystallization.

Crystal data

$[Zn(C_4H_{10}N_4)_3](ClO_4)_2$
$M_r = 606.75$
Trigonal, $P\bar{3}c1$
$a = 9.4496\ (4)$ Å
$c = 15.3237\ (4)$ Å
$V = 1185.01\ (8)$ Å^3
$Z = 2$
$D_x = 1.700$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1664 reflections
$\theta = 2.5$–27.5°
$\mu = 1.33$ mm^{-1}
$T = 110\ (2)$ K
Needle, light yellow
0.35 × 0.10 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.654$, $T_{max} = 0.879$
6818 measured reflections
893 independent reflections
705 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 12$
$k = -10 \rightarrow 10$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.090$
$S = 0.98$
893 reflections
57 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 2.7971P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—N3	2.158 (2)	C4—C5	1.492 (3)
N2—N3	1.386 (3)	C4—C4^{i}	1.502 (5)
N3—C4	1.281 (3)		
N3^{i}—Zn1—N3^{ii}	93.31 (7)	N3^{iii}—Zn1—N3^{iv}	160.52 (11)
N3^{iii}—Zn1—N3	102.24 (11)	N3—Zn1—N3^{iv}	93.30 (7)
N3^{i}—Zn1—N3	74.33 (11)		
N2—N3—C4—C5	5.4 (4)	N2—N3—C4—C4^{i}	−174.1 (2)

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

The amine H atoms were located in a difference Fourier map and their displacement parameters were refined as riding in their as-found relative positions, with isotropic displacement parameters. Methyl H atoms were placed in idealized positions, with C—H = 0.98 Å, and refined using a riding model, with $U_{iso}(H) = 1.5U_{eq}(C)$. The methyl group was allowed to rotate about the C—CH_3 bond, while preserving the C—H bond distances and tetrahedral geometry.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

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