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Bis[3-(*o*-methoxyphenyl)-1-methyltriazene 1-oxidato-*O*,N^3,*O*′]zinc(II)

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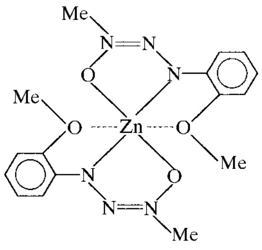
In the title compound, $[Zn(C_8H_{10}N_3O_2)_2]$, the Zn atom displays a highly distorted octahedral coordination involving O and N atoms of two bidentate planar ligands approximately orthogonal to each other; the dihedral angle between the ligand planes is 84.95 (4)°. The ligand molecules show great asymmetry in their bonding to the Zn^{2+} ion, with Zn—O bond distances ranging between 2.056 (2) and 2.534 (2) Å. The planar phenyl ring and the trigonal–planar geometry about the triazene N atom bonded to the phenyl ring suggest a resonance interaction extending over adjacent atoms.

Comment

Substituted triazenes/triazene 1-oxides are potential bidentate ligands forming both bis- and tris-chelate complexes with various metal ions (Rodriguez *et al.*, 1999). The molecular conformations of bis-chelate complexes are extremely sensitive to the nature of substituents in the 1-N and 3-N positions of the triazene moiety. The crystal structures of $[Co(ept)_2]$ (ept is 1-ethyl-3-phenyltriazene 1-oxide; Rudolf *et al.*, 1988) and $[Ni(enpt)_2]$ [enpt is 1-ethyl-3-(*p*-nitrophenyl)triazene 1-oxide; Ciunik *et al.*, 1991] reveal square-planar metal coordination geometry, with the two ligands in a *trans* configuration. The complexes $M(cpmt)_2$ [M = Cd or Zn; cpmt is 3-(*o*-carboxyphenyl)-1-methyltriazene 1-oxide] are, however, reported to be polymeric on the basis of spectroscopic data (Constable, 1984). As part of systematic studies on the synthesis and characterization of triazene 1-oxide derivatives and their metal complexes (Samanta *et al.*, 1998), and to build up a hierarchy for such systems, the structure determination of the title complex, (I), was undertaken.

The crystal structure of (I) (Fig. 1) consists of discrete neutral $[ZnL_2]$ molecules [L is 3-(*o*-methoxyphenyl)-1-methyltriazene 1-oxide]. The two bidentate triazene 1-oxide ligands are bonded to the Zn^{2+} ion through their N and O atoms. The Zn—N distances [1.974 (2) and 1.978 (2) Å] are comparable with corresponding values reported in the literature (Tatar *et al.*, 1999). The coordination of the Zn^{2+} ion by the two phenolate O atoms of the ligands is substantially weakened. This is reflected in the significant lengthening of the Zn—O(phenolate) distances [2.491 (2) and 2.534 (2) Å] compared with the Zn—O(oxide) bond lengths [2.056 (2) and 2.066 (2) Å], and is evidently due to steric hindrance between the essentially planar ligands. The Zn—O distances in bidentate Zn^{II} complexes vary over a wide range and values as different as 1.932 (2) and 2.460 (2) Å have been reported (Kremer-Aach *et al.*, 1997) where the ligand shows great asymmetry in its bonding to the metal.



(I)

The Zn^{2+} ion coordination in (I) is highly distorted octahedral, with the N1, N4, O3 and O4 atoms defining the equatorial plane [maximum deviation for atom N4 of 0.028 (1) Å], and the O1 and O2 atoms occupy the axial sites; the Zn atom is displaced by 0.252 (1) Å towards O2. The distortion of the metal coordination sphere from octahedral geometry is revealed in the large variation of N/O—Zn—N/O *cisoid* [68.92 (8)–118.62 (8)°] and *transoid* [145.89 (9)–155.58 (9)°] angles from their ideal values. This is consistent with the fact that the metal coordination sphere in zinc(II) complexes has been exceptionally flexible and easily adaptable to the demands of the ligands. In the absence of crystal field stabilization effects, the stereochemistry of the ligands around the metal ion is determined essentially by size and electrostatic and covalent bonding forces, and the zinc coordination polyhedra show large deviations from regular geometries (Mangani *et al.*, 1992). A comparison of geometrical parameters of different octahedral Zn^{II} complexes with N,O-donor atoms is given Table 2.

The five-membered chelate rings, *i.e.* Zn—N1—N2—N3—O2 and Zn—N4—N5—N6—O4, are essentially planar, with the maximum deviation of an in-plane atom being 0.036 (1) Å for N1. The two planar ligand molecules, *A* (N1–N3, O1, O2, C1–C8) and *B* (N4–N6, O3, O4, C9–C16), with r.m.s. deviations of 0.066 and 0.030 Å, respectively, are approximately orthogonal to each other, the dihedral angle between *A* and *B* is 84.95 (4)°. The N1 and N4 atoms, with bond angles summing to 360.0 (2) and 359.9 (2)°, respectively, are sp^2 hybridized. Each displays trigonal–planar bonding geometry and coplanarity with the phenyl group, strongly suggesting a resonance interaction extending to the adjacent atoms. This is reflected in the shorter N1—C7 [1.405 (3) Å] and N4—C15 [1.400 (3) Å] bond lengths compared with N3—C8 [1.454 (3) Å] and N6—C16 [1.450 (3) Å]. The short N2—N3 and N5—N6 distances [1.282 (3) and 1.275 (3) Å] indicate double-bond character, and the N1—N2 and N4—N5 bonds [1.318 (3) and

1.314 (3) Å] are shorter than pure single bonds. Similar observations have been reported for other substituted triazene 1-oxide compounds (Samanta *et al.*, 1998).

Discrete monomeric molecules of (I) are held together in the crystal by van der Waals interactions. The minimum distances between two non-H atoms in neighbouring molecules are C16···O2, C5···O4, C8···O4 and C16···O4 with values of 3.227 (3), 3.431 (4), 3.498 (4) and 3.514 (4) Å, respectively.

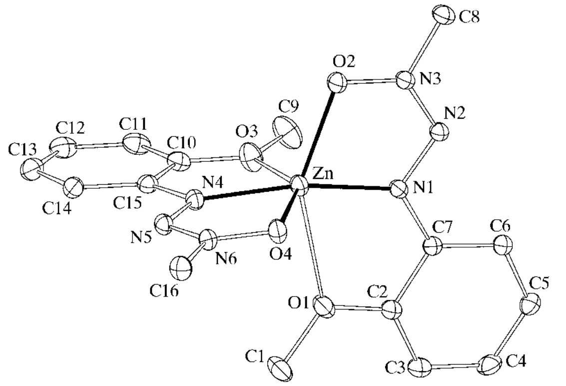


Figure 1
The molecular structure of (I) shown with 50% probability displacement ellipsoids.

Experimental

The title compound was prepared following the procedure of Kumar *et al.* (1983). Single crystals were obtained by slow evaporation from hexane.

Crystal data

$[Zn(C_8H_{10}N_3O_2)_2]$
$M_r = 425.75$
Triclinic, $P\overline{1}$
$a = 10.853$ (1) Å
$b = 11.547$ (1) Å
$c = 7.821$ (1) Å
$\alpha = 96.97$ (1)°
$\beta = 110.03$ (1)°
$\gamma = 86.84$ (1)°
$V = 913.9$ (2) Å^3
$Z = 2$
$D_x = 1.547$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 34.5$–39.3°
$\mu = 2.187$ mm^{-1}
$T = 293$ (2) K
Block, light yellow
0.30 × 0.25 × 0.15 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.605$, $T_{max} = 0.718$
3819 measured reflections
3622 independent reflections
3194 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 78.02°$
$h = -7 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -9 \rightarrow 9$
3 standard reflections every 150 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.122$
$S = 0.966$
3622 reflections
248 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0838P)^2 + 0.3895P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn—N1	1.974 (2)	Zn—O1	2.491 (2)
Zn—N4	1.978 (2)	N1—N2	1.318 (3)
Zn—O4	2.056 (2)	N2—N3	1.282 (3)
Zn—O3	2.534 (2)	N4—N5	1.314 (3)
Zn—O2	2.066 (2)	N5—N6	1.275 (3)
N1—Zn—N4	155.58 (9)	O2—Zn—O1	147.19 (7)
N1—Zn—O4	118.62 (8)	O3—Zn—N4	68.92 (8)
N4—Zn—O4	77.75 (7)	O3—Zn—N1	91.25 (8)
N1—Zn—O2	77.33 (7)	O3—Zn—O4	145.89 (9)
N4—Zn—O2	118.02 (8)	O1—Zn—O3	81.70 (8)
O4—Zn—O2	104.56 (8)	O2—Zn—O3	97.44 (8)
N1—Zn—O1	69.91 (7)	N2—N1—Zn	117.3 (2)
N4—Zn—O1	92.46 (8)	N5—N4—Zn	116.6 (2)
O4—Zn—O1	92.96 (8)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5*A*···O4^{i}	0.93	2.89	3.431 (4)	118
C8—H8*A*···O4^{ii}	0.96	2.61	3.498 (4)	154
C16—H16*C*···O2^{iii}	0.96	2.68	3.227 (3)	117
C16—H16*C*···O4^{iii}	0.96	2.69	3.514 (4)	144

Symmetry codes: (i) $-x, -y, -z$; (ii) $x, y, 1 + z$; (iii) $-x, 1 - y, -z$.

Table 3
Geometric parameters (Å,°) of octahedral Zn^{II} complexes with N- and O-donor atoms.

	Coordination polyhedron	Zn–N	Zn–O	N/O–Zn–N/O (*cis*)	N/O–Zn–N/O (*trans*)
(I)^a	N_2O_4	1.974 (2)	2.056 (2)	68.92 (8)	145.89 (9)
		−1.978 (2)	−2.534 (2)	−118.62 (8)	−155.58 (9)
(II)^b	N_2O_4	2.136 (3)	2.083 (2)	77.4 (1)	167.1 (1)
		−2.156 (3)	−2.130 (2)	−100.5 (1)	−171.8 (1)
(III)^c	NO_5	2.146 (4)	1.977 (4)	74.3 (1)	156.7 (1)
		−2.148 (4)	−2.440 (3)	−101.5 (1)	−170.3 (2)
(IV)^d	N_4O_2	2.121 (5)	2.155 (4)	59.0 (1)	151.7 (1)
		−2.131 (4)	−2.246 (4)	−110.2 (2)	−172.9 (2)
(V)^e	N_3O_3	2.027 (7)	2.015 (6)	70.8 (2)	155.8 (2)
		−2.389 (7)	−2.245 (6)	−109.1 (2)	−166.2 (3)
(VI)^f	N_4O_2	2.042 (4)	2.473 (3)	72.8 (1)	127.7 (2)
		−2.100 (4)	−2.639 (3)	−109.1 (2)	−175.5 (1)

Notes: (*a*) this work; (*b*) Zhang *et al.* (1999); (*c*) Sakiyama *et al.* (1999); (*d*) Chen *et al.* (1994); (*e*) Nakai *et al.* (1999); (*f*) Tulchinsky *et al.* (1990).

All H atoms were placed in calculated positions, each riding on their carrier atoms with an isotropic displacement parameter of 1.5 (for methyl H atoms) or 1.2 (for the other H atoms) times the equivalent isotropic displacement parameter of the attached atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1995); software used to prepare material for publication: *SHELXL*97 and *PARST*95 (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1370). Services for accessing these data are described at the back of the journal.

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