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[3,3′-Iminobis(*N*,*N*-dimethylpropylamine)](4′-methoxyflavonolato)zinc(II) perchlorate, [Zn(4′-MeOfla)(idpaH)]ClO_4†

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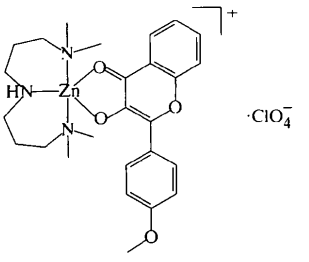
Abstract

The title compound, $[Zn(C_{16}H_{11}O_4)(C_{10}H_{25}N_3)]ClO_4$, contains a cationic five-coordinate zinc(II) complex with distorted trigonal-bipyramidal geometry. Two N atoms of the tridentate 3,3′-iminobis(*N*,*N*-dimethylpropylamine) (idpaH) ligand and one O atom of the 4′-methoxyflavonolate (4′-MeOfla) ligand occupy basal positions, the other O atom of the flavonolate ligand and one N atom of the idpaH ligand being in apical positions.

Comment

Copper(I) and copper(II) complexes of flavonol, as structural and functional models of the Cu^{II}-containing dioxygenase quercetinase, have been reported (Speier *et al.*, 1990; Balogh-Hergovich *et al.*, 1991; Lippai *et al.*, 1997). Zinc and cadmium derivatives have also been prepared by electrochemical synthesis (Annan *et al.*, 1990). The flavonolate ligand (fla) coordinates metals through its 3-hydroxy and 4-carbonyl groups. We report here the preparation and crystal structure of a zinc(II) 4′-methoxyflavonolate, (I), with the nitrogen-containing ligand 3,3′-iminobis(*N*,*N*-dimethylpropylamine) in order to study model reactions of a non-redox metal system.



(I)

The geometry around the zinc(II) centre in compound (I) is approximately trigonal bipyramidal, with τ = 0.76. For perfect square-pyramidal and trigonal-bipyramidal geometries, the values of τ are zero and unity, respectively, τ being an index of the degree of trigonality within the structural continuum between square-pyramidal and trigonal-bipyramidal geometries (Addison *et al.*, 1984). Two N atoms of the tridentate idpaH ligand, with Zn—N distances of 2.148 (4) and 2.115 (3) Å, and the O atom of the 3-hydroxy group of the 4′-methoxyflavonolate ligand occupy basal positions. The O atom of the 4-carbonyl group of the flavonolate and the N atom of the idpaH ligand, with a Zn—N distance of 2.151 (3) Å, are in apical positions.

The Zn—O bond distance of the 4-carbonyl O atom is shorter [Zn—O2 2.154 (3) Å] than that found in the only other known zinc(II) flavonolate complex, namely $[Zn(fla)_2(tmeda)]$ [2.240 (1) Å; Annan *et al.*, 1990; tmeda is *N*,*N*,*N*′,*N*′-tetramethylenediamine], and

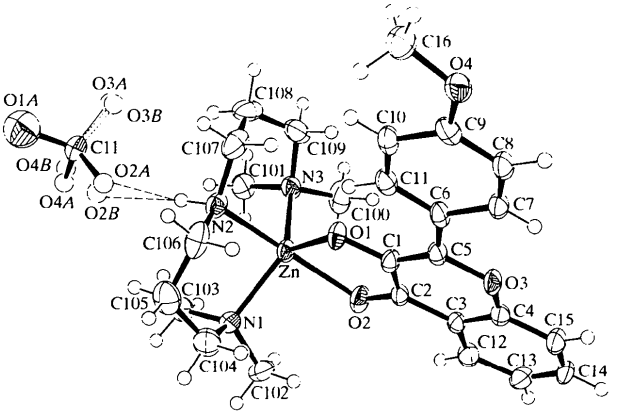


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

† Alternative name: [3,3′-iminobis(*N*,*N*-dimethylpropylamine-*N*)][2-(4-hydroxyphenyl)-4-oxo-4*H*-chromen-3-olato-O^3,O^4)zinc(II) perchlorate.

that of the 3-hydroxy O atom is similar [Zn—O1 1.992 (3) Å] to that in $[Zn(fla)_2(tmeda)]$ [1.980 (1) Å]. However, both Zn—O bond distances are considerably longer than the corresponding Cu—O distances in $[Cu(bpy)(fla)]ClO_4$ [1.970 (3) and 1.897 (3) Å; Lippai *et al.*, 1997; bpy is 2,2′-bipyridyl].

There is weak N—H···O hydrogen bonding between the disordered O2 atom of the perchlorate anion and the N2 atom of the idpaH ligand.

Experimental

The title compound was prepared by stirring $Zn(ClO_4)_2·6H_2O$ with equimolar amounts of 3,3′-iminobis(*N*,*N*-dimethylpropylamine) and 4′-methoxyflavonol in toluene–ethanol (1:1) at 333 K under N_2 for 3 h. Recrystallization from acetone gave crystals suitable for X-ray measurements.

Crystal data

$[Zn(C_{16}H_{11}O_4)(C_{10}H_{25}N_3)]ClO_4$
M_r = 619.40
Orthorhombic
Pbca
a = 31.425 (5) Å
b = 14.289 (2) Å
c = 12.375 (2) Å
V = 5556.8 (15) Å^3
Z = 8
D_x = 1.481 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 26 reflections
θ = 2.27–25.50°
μ = 1.033 mm^{-1}
T = 293 (2) K
Block
0.50 × 0.30 × 0.30 mm
Yellow

Data collection

Siemens (Nicolet Syntex) diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.579, T_{max} = 0.734
5004 measured reflections
5004 independent reflections

3513 reflections with $I > 2\sigma(I)$
θ_{max} = 25.5°
$h = 0 \rightarrow 38$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 14$
3 standard reflections every 50 reflections
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.104
S = 1.123
5004 reflections
388 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0163P)^2 + 13.5851P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.010
$\Delta\rho_{max}$ = 0.341 e Å^{-3}
$\Delta\rho_{min}$ = −0.398 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zn—O1	1.992 (3)	Zn—O2	2.154 (3)
Zn—N3	2.115 (3)	O1—C1	1.332 (5)
Zn—N1	2.148 (4)	O2—C2	1.279 (5)
Zn—N2	2.151 (3)		
O1—Zn—N3	113.18 (13)	O1—Zn—O2	79.94 (12)
O1—Zn—N1	126.45 (13)	N3—Zn—O2	99.09 (13)
N3—Zn—N1	120.35 (14)	N1—Zn—O2	92.76 (13)
O1—Zn—N2	87.40 (12)	N2—Zn—O2	165.86 (12)
N3—Zn—N2	91.65 (14)	C1—O1—Zn	114.4 (3)
N1—Zn—N2	89.68 (14)	C2—O2—Zn	109.2 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···O2*A*	0.95	1.93	2.857 (15)	166.1
N2—H2N···O2*B*	0.95	2.13	3.07 (2)	171.3

The perchlorate ion is disordered. Three O atoms appear in six partially occupied positions (O2*A*/O3*A*/O4*A* and O2*B*/O3*B*/O4*B*). The two positions are obtained by rotation (*ca* 15.5°) of the perchlorate ion around the O1*A*—Cl axis.

Data collection: local diffractometer software. Cell refinement: local diffractometer software. Data reduction: local diffractometer software. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1294). Services for accessing these data are described at the back of the journal.

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