

(Acetato- κO)[tris(3,5-dimethylpyrazol-1-yl- κN^2)hydroborato]zinc(II)

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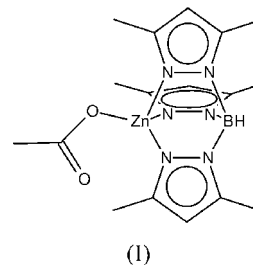
The title complex, $[\text{Zn}(\text{C}_{15}\text{H}_{22}\text{BN}_6)(\text{C}_2\text{H}_3\text{O}_2)]$ or $(\text{Tp}^{\text{Me,Me}})\text{-Zn}(\text{OAc})$, contains a tripodal tris(pyrazolyl)hydroborate ligand, a monodentate acetate ligand and a Zn^{II} centre in a distorted tetrahedral coordination environment capped on one triangular face by a secondary $\text{Zn} \cdots \text{O}$ interaction with the second O atom of the acetate ligand. The four-coordination of Zn^{II} and the essentially monodentate character of the acetate ligand are due to the high steric demands of the ligand set, which prevent chelate formation and five-coordination and lead to relatively long $\text{Zn}-\text{O}$ and $\text{Zn}-\text{N}$ bonds compared with related complexes of Zn^{II} and other metals.

Comment

Metal complexes containing tris(pyrazolyl)hydroborate ligands, *viz.* $\text{Tp}^{\text{R,R'}}$ or $[\text{HB}(3\text{-R},5\text{-R'}\text{Pz})_3]^-$ ($\text{R/R'} = \text{H}$, alkyl or aryl), have been investigated widely by inorganic, organometallic and bioinorganic chemists (Trofimenko, 1993, 1999; Kitajima & Tolman, 1995). This popularity has resulted from their ease of preparation and their wide variation in steric and electronic properties by the use of different substituents on the pyrazole rings. Numerous studies have been performed to synthesize stable tetrahedral $\text{MX}(\text{Tp}^{\text{R,R'}})$ metal complexes ($\text{M} = \text{Zn}$, Cd , Cu ; $\text{X} = \text{Cl}$, OAc) by the use of these sterically demanding tridentate N -donor ligands to model the structure and function of the active site of the carbonic anhydrase enzyme (Guo *et al.*, 1998; Vahrenkamp, 1999; Looney *et al.*, 1993). The title complex, (I), has been prepared as one such model, and its structure has been determined to confirm the tetrahedral coordination and monomeric formulation. The molecular structure of (I) is shown in Fig. 1, and selected bond lengths and angles are given in Table 1.

Zn^{II} , as a d^{10} ion without a crystal field stabilization energy preference for any particular coordination geometry, exhibits a very flexible and varied coordination chemistry. The most

common coordination numbers are 4, 5 and 6, represented by structures in the approximate ratio 2:1:1 in the Cambridge Structural Database (CSD, Version 5.30 with updates to May 2009; Allen, 2002). Tetrahedral coordination (regular or distorted) is promoted by bulky ligands, including substituted $\text{Tp}^{\text{R,R'}}$ ligands, as in the case of complex (I). Here the primary coordination is distorted tetrahedral, with an essentially regular tripodal arrangement for $\text{Tp}^{\text{Me,Me}}$ and a monodentate acetate ligand; the $\text{Zn1}-\text{O1}$ bond length is 1.9217 (17) Å, while the nonbonded $\text{Zn1} \cdots \text{O2}$ distance is 2.6033 (18) Å.



(I)

Complex (I) is almost isostructural with the corresponding Ni^{II} complex (Hikichi *et al.*, 2002), and there is an r.m.s. deviation of only 0.028 Å for a least-squares overlay of the two MN_6B units. However, the nickel complex is clearly five-coordinate, with a more nearly symmetrically chelating acetate ligand, giving $\text{Ni}-\text{O}$ bond lengths of 2.014 (3) and 2.131 (4) Å, a difference of only 0.117 Å, compared with 0.681 Å for the title zinc complex. Of the 25 $(\text{Tp}^{\text{R,R'}})\text{Zn}(\text{carboxylate})$ complexes in the CSD, 19 have a monodentate carboxylate ligand, five are chelate complexes and one contains both geometries.

As an alternative description, if the weaker but not insignificant secondary $\text{Zn1} \cdots \text{O2}$ interaction is included, the coordination of Zn1 is monocapped tetrahedral, this interaction capping the N2/N4/O1 triangular face. The distortion of the tetrahedral geometry by the capping atom O2 is towards

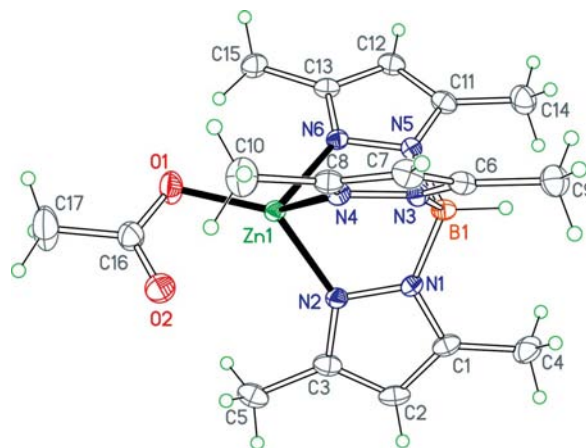


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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trigonal bipyramidal, with atoms N2, N4 and O1 in the equatorial plane, and atoms N6 and O2 in axial sites. It might be expected that strengthening of the secondary Zn \cdots O interaction relative to the primary Zn—O bond would tend to equalize the two carboxylate C—O bond lengths, the carboxylate group being delocalized as a symmetrical chelate ligand and having essentially localized single (coordinated O) and double (uncoordinated O) C—O bonds in monodentate mode, but an analysis of relevant four- and five-coordinate zinc complexes with acetate ligands in the CSD (of which there are approximately 100), using the CSD *VISTA* tool, shows only weak correlation. Indeed, there are numerous cases in which the C—O bonds have relative lengths opposite to the expected pattern, with what appears on this criterion to be the carbonyl O atom coordinated to Zn1. In the title zinc complex, which we prefer to describe as primarily tetrahedral with significant distortion through a secondary capping interaction, the difference in C—O bond lengths of 0.070 Å is not much greater than in the corresponding nickel complex (0.056 Å), which is certainly better described as five-coordinate with two Ni—O bonds of similar strength. Irregular and intermediate coordination geometries are, of course, very much a matter of interpretation.

Although there are over 3000 known structures of metal complexes with Tp^{R,R'} ligands, of which almost 300 are zinc complexes, and nearly one-third of the metal complexes contain specifically the Tp^{Me,Me} ligand featured here, only four zinc complexes of Tp^{Me,Me} have been reported previously. Of these, two are octahedral Zn(Tp^{Me,Me})₂, one of them unsolvated (Looney *et al.*, 1995) and the other a toluene solvate (Yang *et al.*, 1997), and the other two are (Tp^{Me,Me})ZnCl and (Tp^{Me,Me})ZnMe (Bonitatebus & Armstrong, 1999), both tetrahedral. There are 189 four-coordinate (Tp^{R,R'})ZnL structures in the CSD (*L* is any monodentate ligand), in 69 of which *L* coordinates to Zn through an O atom. The range of Zn—O bond lengths in these 69 structures is 1.793–1.977 Å, with a mean of 1.879 Å. The Zn1—O1 bond in the title complex is one of the longest of these, at 1.9217 (17) Å, while complexes with the shortest Zn—O bonds include hydroxy complexes (Tp^{R,R'})ZnOH (Alsasser *et al.*, 1991; Ruf & Vahrenkamp, 1996). This, together with the fact that the Zn—N bonds here are marginally longer than the corresponding Ni—N bonds in the nickel(II) analogue (Hikichi *et al.*, 2002), despite the smaller normal covalent radius of Zn^{II} compared with Ni^{II}, is a clear indication of the steric hindrance of the ligands in the title complex, which we have suggested as being responsible for the four- rather than five-coordination in this case.

There are a few C—H \cdots O contacts below the sum of van der Waals radii that could represent weak interactions. Of these, the most significant in terms of its structural consequence is the intramolecular C15—H15A \cdots O1 contact (H15A \cdots O1 = 2.55 Å, C15 \cdots O1 = 3.45 Å and C15—H15A \cdots O1 = 152°), which brings this C15 methyl group into an eclipsed conformation relative to the adjacent ring C—N bond, while the remaining five pyrazole methyl substituents are staggered as expected.

Experimental

Zinc acetate dihydrate (0.1 g, 0.45 mmol) and potassium tris(3,5-dimethylpyrazolyl)hydroborate (0.153 g, 0.45 mmol; Trofimenko, 1967) were added to acetone (30 ml). The mixture was stirred for 6 h and then evaporated to dryness *in vacuo*. The residue was washed with diethyl ether (2 \times 5 ml) and *n*-pentane (2 \times 5 ml) and air-dried to give a white powder (0.123 g, 72% based on Zn). Colourless single crystals of the title complex, (I), were obtained from an acetone solution by slow evaporation of the solvent at room temperature. The air-stable crystals of (I) are slightly soluble in common organic solvents such as acetone, acetonitrile, dimethylformamide and dimethyl sulfoxide.

The FT-IR spectrum of (I) exhibits a medium-intensity feature at 2532.85 cm⁻¹, characteristic of the stretching vibration of the B—H bond in the Tp^{Me,Me} ligand. It is difficult to identify features due to the asymmetric and symmetric vibrations of the coordinated acetate, because the Tp^{Me,Me} ligand gives vibrational bands in the same regions.

Crystal data

[Zn(C ₁₅ H ₂₂ BN ₆)(C ₂ H ₃ O ₂)]	<i>V</i> = 1957.2 (9) Å ³
<i>M_r</i> = 421.61	<i>Z</i> = 4
Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 13.766 (4) Å	<i>μ</i> = 1.28 mm ⁻¹
<i>b</i> = 7.721 (2) Å	<i>T</i> = 150 K
<i>c</i> = 19.031 (5) Å	0.40 \times 0.30 \times 0.14 mm
<i>β</i> = 104.630 (4)°	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	14905 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	3835 independent reflections
<i>T</i> _{min} = 0.630, <i>T</i> _{max} = 0.845	3441 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.030

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.033	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> (<i>F</i> ²) = 0.081	$\Delta\rho_{\text{max}}$ = 0.38 e Å ⁻³
<i>S</i> = 1.16	$\Delta\rho_{\text{min}}$ = -0.62 e Å ⁻³
3835 reflections	
255 parameters	

Table 1

Selected geometric parameters (Å, °).

Zn1—N2	2.0165 (19)	Zn1—O1	1.9217 (17)
Zn1—N4	2.0104 (19)	O1—C16	1.291 (3)
Zn1—N6	2.0511 (18)	O2—C16	1.221 (3)
N2—Zn1—N4	93.14 (7)	N4—Zn1—O1	126.80 (8)
N2—Zn1—N6	92.29 (7)	N6—Zn1—O1	109.06 (7)
N4—Zn1—N6	92.99 (7)	Zn1—O1—C16	106.21 (15)
N2—Zn1—O1	131.78 (8)	O1—C16—O2	122.0 (2)

H atoms were located in a difference map. The H atom bonded to B1 was refined freely. The remaining H atoms were idealized and refined with a riding model, including free rotation about C—C bonds, with C—H = 0.95–0.98 Å and *U*_{iso}(H) = 1.5*U*_{eq}(C) or 1.2*U*_{eq}(ring C).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine

structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3023). Services for accessing these data are described at the back of the journal.

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