C(21)	−0.1735 (9)	0.0792 (8)	0.3112 (10)	4.3 (2)
C(22)	−0.2978 (9)	0.0431 (8)	0.2131 (10)	4.9 (2)
C(23)	−0.3634 (10)	−0.0238 (10)	0.3262 (10)	7.7 (3)
C(24)	−0.4779 (10)	−0.0721 (10)	0.2297 (20)	10.0 (4)
C(31)	0.0507 (9)	0.1894 (7)	0.3201 (10)	4.2 (2)
C(32)	0.1555 (10)	0.2317 (8)	0.2270 (10)	5.7 (3)
C(33)	0.2664 (10)	0.2643 (10)	0.3455 (10)	7.1 (3)
C(34)	0.3699 (10)	0.3053 (10)	0.255 (2)	9.6 (4)

Table 2. *Selected geometric parameters* (Å, °)

Ni—S	2.217 (2)	P—C(11)	1.825 (7)
Ni—P	2.245 (2)	P—C(21)	1.848 (8)
S—C(1)	1.754 (8)	P—C(31)	1.855 (7)
S—Ni—S^i	180	Ni—S—C(1)	108.4 (3)
S—Ni—P	86.29 (8)	Ni—P—C(11)	119.1 (2)
S—Ni—P^i	93.71 (8)	Ni—P—C(21)	108.1 (3)
P—Ni—P^i	180	Ni—P—C(31)	116.4 (3)

Symmetry code: (i) $-x, -y, -z$.

Intensity data used in the refinements were corrected for Lorentz–polarization factors, linear decay and absorption based on ψ scans and refinement from ΔF (*DIFABS*; Walker & Stuart, 1983). All non-H atoms were refined with anisotropic displacement parameters.

Data collection and refinement: *CONTROL* (Molecular Structure Corporation, 1988). Data reduction: *SDP/VAX* (Enraf–Nonius, 1989). Structure solution: direct methods using *MULTAN*11/82 (Main *et al.*, 1982). Structure refinement: *LSFM* (B. A. Frenz & Associates Inc., 1985). Molecular graphics: *ORTEP*II (Johnson, 1976). Preparation of material for publication: *SDP/VAX*.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BK1083). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Benzoato[hydrotris(3-phenylpyrazol-1-yl-N^2)borato]zinc(II)

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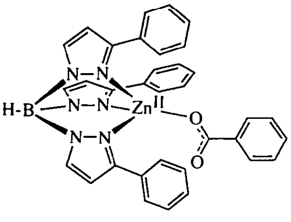
Abstract

The structure of the title complex, [Zn{HB($C_9H_7N_2$)$_3$}-($C_7H_5O_2$)], has been determined; the central Zn atom is coordinated in a distorted tetrahedral environment by three N atoms, one from each pyrazole ring [Zn—N 2.038 (5)–2.084 (5) Å], and by a benzoate O atom [Zn—O 1.935 (5) Å]. A hydrophobic pocket is formed around the fourth coordination site of the Zn atom by the phenyl substituent on each pyrazole ring; this pocket is occupied by the benzoate ligand.

Comment

Since the active site of carbonic anhydrase comprises a Zn^{II} atom coordinated to three histidine imidazole groups, the use of hydrotris(pyrazol-1-yl)borato ligands has become increasingly popular in synthetic inorganic and bioinorganic chemistry (Trofimenko, 1993). In recent reports, significantly bulky ligands such as hydrotris[(3-phenyl- or *tert*-butyl)pyrazol-1-yl]borato (*L*), will allow [Zn*L*]$^+$ formation (Trofimenko, Calabrese & Thompson, 1987; Looney, Han, McNeill & Parkin, 1993; Alfasser, Ruf, Trofimenko & Vehrenkamp, 1993), while the most commonly used of such ligands, hydrotris(3,5-dimethyl or unsubstituted pyrazolyl)borato (*L*′), will form Zn*L*′$_2$. Since the Zn^{II} in the biological system is almost always coordinated in a tetrahedral fashion, [Zn*L*]$^+$ is much more interesting, and the fourth, the ‘mformat a: functional’, site can be occupied by a small ligand, such as water, *R*—COO$^-$, OH$^-$ or NO_3^-. This work reports the synthesis and crystal structure of novel benzoato[hydrotris(3-phenylpyrazol-1-yl)borato]zinc(II), (I), where the fourth ligand is a benzoate ion.

Fig. 1 shows the molecular structure of [Zn{HB(3-Phpz)$_3$}(OBz)]. Each distance between the central Zn^{II} and the three N-atom sites in the tridentate ligand HB(3-Phpz)$_3^-$ is longer than the distance between Zn and O of the monodentate benzoate ion (see Table 2) by *ca* 0.1 Å. All values of the N—Zn—N bond angles range between 90.0 (2) and 97.0 (2)°, and those of N—Zn—O from 113.4 (2) to 131.3 (2)°. Thus, the geometry around



(I)

Zn^{II} is quite distorted from ideal tetrahedral by the bite of the ligand. The Zn^{II} has enough space to bind an O atom of a benzoate ligand; its fourth coordination site is located in the hydrophobic pocket created by the substituents, here the phenyl groups, of the pyrazole rings. In general, a central Zn^{II} ion should be kept at roughly equivalent distances from the three N atoms in a bulky tridentate hydrotris(pyrazolyl)borate ligand. When a small unidentate ligand (*e.g.*, *R*—COO$^-$, OH$^-$, CO$_3^{2-}$ or NO$_3^-$) locates at the fourth coordination site in the hydrophobic pocket formed by the *tert*-butyl or phenyl substituent on each pyrazole ring, all the bond distances between Zn^{II} and each N atom in the bulky tridentate hydrotris(pyrazolyl)borate ligand become longer than the bond distance Zn^{II}—O (Han, Gorrell, Looney & Parkin, 1991; Alfasser, Trofimenko, Looney, Parkin & Vehrenkamp, 1991; Alfasser & Vehrenkamp, 1993; Alfasser, Ruf, Trofimenko & Vehrenkamp, 1993; Han, Looney, McNeill, Parkin, Rheingold & Haggerty, 1993; Alfasser, Powell, Trofimenko & Vehrenkamp, 1993). The bond distance between the Zn^{II} atom and the O atom of the small fourth ligand depends on the conformation of the phenyl or *tert*-butyl substituents as well as the size of the hydrophobic pocket.

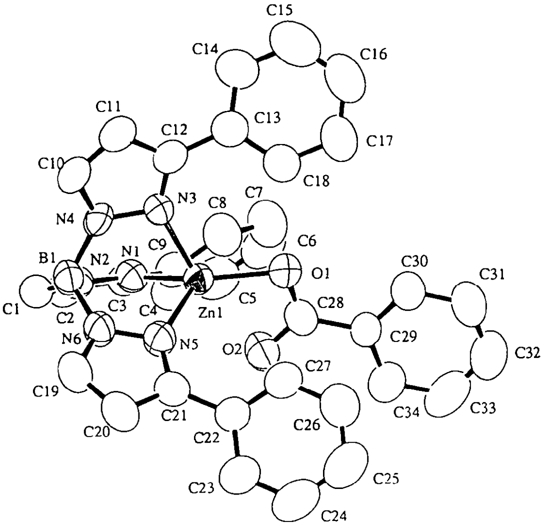


Fig. 1. *ORTEP* (Johnson, 1976) drawing and the atom-numbering system of [Zn{HB(3-Phpz)$_3$}(OBz)]. Ellipsoids are depicted at the 50% probability level.

Experimental

Synthesis and recrystallization were carried out by the reaction of K[HB(3-Phpz)$_3$] and [Zn(C$_6$H$_5$CO$_2$)$_2$] (molar ratio 1:1) in methanol solution.

Crystal data

[Zn(C$_{27}$H$_{22}$BN$_6$)(C$_7$H$_5$O$_2$)]
M_r = 627.82
Triclinic
$P\bar{1}$
a = 12.884 (5) Å
b = 13.675 (6) Å
c = 9.844 (6) Å
α = 104.77 (4)°
β = 111.99 (3)°
γ = 73.95 (4)°
V = 1523 (1) Å^3
Z = 2
D_x = 1.37 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 13 reflections
θ = 22.7–22.9°
μ = 1.451 mm^{-1}
T = 293 K
Prismatic
0.30 × 0.20 × 0.07 mm
Colourless

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min}$ = 0.81, $T_{\max}$ = 1.00
4111 measured reflections
3836 independent reflections

2338 observed reflections [$I > 5\sigma(I)$]
$R_{\rm int}$ = 0.017
$\theta_{\max}$ = 55°
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -10 \rightarrow 0$
3 standard reflections monitored every 150 reflections intensity decay: 0.44%

Refinement

Refinement on F
R = 0.051
wR = 0.083
S = 2.38
2338 reflections
398 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.001225F^2]$
$(\Delta/\sigma)_{\max}$ = 0.01

$\Delta\rho_{\max}$ = 0.35 e Å^{-3}
$\Delta\rho_{\min}$ = −0.44 e Å^{-3}
Extinction correction: Zachariasen (1967) Type 2 Gaussian isotropic
Extinction coefficient: 8.04 (5) × 10^6
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Zn(1)	0.16370 (7)	0.75741 (7)	0.20112 (10)	4.32 (2)
O(1)	0.3148 (4)	0.7590 (4)	0.3452 (6)	5.5 (1)
O(2)	0.2009 (4)	0.7861 (4)	0.4785 (6)	6.3 (1)
N(1)	0.0552 (4)	0.6589 (4)	0.1485 (6)	4.6 (1)
N(2)	−0.0422 (5)	0.6859 (4)	0.0370 (6)	4.6 (1)
N(3)	0.1619 (4)	0.7247 (4)	−0.0184 (6)	4.2 (1)
N(4)	0.0523 (5)	0.7320 (4)	−0.1148 (6)	4.4 (1)
N(5)	0.0416 (5)	0.8883 (4)	0.1656 (6)	4.8 (1)
N(6)	−0.0493 (4)	0.8713 (4)	0.0404 (7)	4.9 (1)
C(1)	−0.1187 (6)	0.6325 (6)	0.0251 (8)	4.9 (2)
C(2)	−0.0709 (6)	0.5690 (6)	0.1284 (9)	5.2 (2)

C(3)	0.0400 (6)	0.5867 (5)	0.2055 (8)	4.5 (2)
C(4)	0.1324 (6)	0.5343 (5)	0.3181 (9)	5.1 (2)
C(5)	0.1082 (5)	0.4858 (6)	0.407 (1)	6.6 (2)
C(6)	0.194 (1)	0.4308 (7)	0.507 (1)	8.0 (3)
C(7)	0.303 (1)	0.4238 (7)	0.523 (1)	7.8 (3)
C(8)	0.3303 (8)	0.4703 (7)	0.437 (1)	8.0 (3)
C(9)	0.2453 (7)	0.5253 (6)	0.333 (1)	6.4 (2)
C(10)	0.0530 (6)	0.7092 (5)	−0.2524 (8)	5.1 (2)
C(11)	0.1633 (7)	0.6856 (5)	−0.2493 (8)	5.2 (2)
C(12)	0.2299 (6)	0.6962 (5)	−0.1016 (8)	4.6 (2)
C(13)	0.3549 (6)	0.6800 (5)	−0.0420 (9)	5.2 (2)
C(14)	0.4225 (8)	0.6124 (7)	−0.118 (1)	7.3 (3)
C(15)	0.541 (1)	0.6000 (9)	−0.059 (2)	9.5 (4)
C(16)	0.5914 (9)	0.654 (1)	0.074 (1)	9.4 (4)
C(17)	0.5262 (8)	0.7230 (10)	0.154 (1)	8.1 (3)
C(18)	0.4092 (6)	0.7359 (7)	0.0943 (9)	6.0 (2)
C(19)	−0.1307 (6)	0.9573 (6)	0.0283 (10)	5.9 (2)
C(20)	−0.0924 (6)	1.0329 (5)	0.148 (1)	6.3 (2)
C(21)	0.0157 (6)	0.9871 (5)	0.2306 (8)	5.0 (2)
C(22)	0.0932 (6)	1.0343 (5)	0.3688 (8)	4.7 (2)
C(23)	0.0481 (7)	1.0994 (6)	0.4767 (9)	6.0 (2)
C(24)	0.118 (1)	1.1455 (7)	0.607 (1)	7.3 (3)
C(25)	0.232 (1)	1.1272 (8)	0.632 (1)	8.3 (3)
C(26)	0.2783 (6)	1.0633 (7)	0.527 (1)	7.7 (3)
C(27)	0.2088 (7)	1.0179 (6)	0.3956 (9)	5.8 (2)
C(28)	0.2967 (6)	0.7835 (5)	0.4716 (9)	5.0 (2)
C(29)	0.3927 (6)	0.8094 (5)	0.6032 (8)	4.9 (2)
C(30)	0.4986 (7)	0.8016 (7)	0.5928 (10)	7.0 (2)
C(31)	0.5875 (8)	0.828 (1)	0.719 (1)	9.7 (3)
C(32)	0.5727 (10)	0.8635 (9)	0.853 (1)	8.7 (3)
C(33)	0.468 (1)	0.8726 (8)	0.863 (1)	8.3 (3)
C(34)	0.3784 (7)	0.8463 (7)	0.7405 (10)	6.6 (2)
B(1)	−0.0521 (6)	0.7643 (7)	−0.0580 (10)	5.0 (2)

Table 2. *Selected geometric parameters* (Å, °)

Zn(1)—O(1)	1.935 (5)	O(2)—C(28)	1.252 (8)
Zn(1)—N(1)	2.044 (6)	C(28)—C(29)	1.463 (10)
Zn(1)—N(3)	2.084 (5)	Zn(1)···O(2)	2.534 (6)
Zn(1)—N(5)	2.038 (5)	Zn(1)···B(1)	2.985 (7)
O(1)—C(28)	1.295 (9)	O(1)···B(1)	4.901 (8)
O(1)—Zn(1)—N(1)	131.3 (2)	Zn(1)—O(1)—C(28)	103.5 (4)
O(1)—Zn(1)—N(3)	113.4 (2)	O(1)—C(28)—O(2)	120.9 (7)
O(1)—Zn(1)—N(5)	122.6 (2)	O(1)—C(28)—C(29)	116.6 (6)
N(1)—Zn(1)—N(3)	90.0 (2)	O(2)—C(28)—C(29)	122.5 (7)
N(1)—Zn(1)—N(5)	97.0 (2)	O(1)—Zn(1)···B(1)	169.5 (3)
N(3)—Zn(1)—N(5)	92.1 (2)		

The structure was solved by the direct methods (*SHELXS*86; Sheldrick, 1985) which revealed the position of the Zn atom. The remaining atoms were located by Fourier techniques (*DIRDIF*; Beurskens *et al.*, 1992). The non-H atoms were refined anisotropically by full-matrix least-squares methods, H atoms were located from a difference electron density map, placed in fixed positions (C—H = 0.95, 1.00 Å, B—H = 1.05 Å) but not refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1992). Structure solution: *SHELXS*86; *DIRDIF*. Structure refinement: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1030). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1556–1558

Water-Bridged Molecular Adduct of Tetrabromocadmate(II) with Protonated Dafone (4,5-Diazafluoren-9-one), $(C_{11}H_7N_2O)_2[CdBr_4].2H_2O$

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Abstract

The structure of the title compound, bis($4H^+$-9-oxo-4,5-diazafluorenium) tetrabromocadmate(II)–water (1/2), consists of a distorted tetrahedral $(CdBr_4)^{2-}$ anion and HL^+ cations, where L is the organic ligand dafone (4,5-diazafluoren-9-one). There is no direct bonding between the metal atom and the ligand. The protonation of one of the N atoms in the dafone ring system gives rise to an opening of the C—N—C angle when compared with the corresponding value in the neutral form. The dihedral angles between the mean planes of the pyridine