

C(71)—C(11)—C(21)	122.5 (4)	P(1 ^b)—N(1)—P(1)	149.2 (3)
C(71)—C(11)—C(61)	120.9 (5)	N(1)—P(1)—C(14)	113.7 (2)
C(21)—C(11)—C(61)	116.5 (6)	N(1)—P(1)—C(15)	108.9 (1)
C(31)—C(21)—C(11)	122.4 (6)	N(1)—P(1)—C(16)	108.6 (1)
C(41)—C(31)—C(21)	121.3 (9)		

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

The structure was solved by direct method and refined by full-matrix least-squares techniques to $R = 0.074$ using an Ag₄Cu metal-atom model, with Cu on the twofold axis, non-H atoms anisotropic, H atoms constrained to ride on the appropriate C atoms at a distance of 0.95 Å, fixed isotropic displacement parameters for H atoms in the cation and a common refinable isotropic displacement parameter for H atoms of each phenyl group in the anion. The ΔF map showed a peak of 3.39 e Å⁻³ at a distance of 0.43 Å from the Cu atoms. This, and the metal-carbon bond lengths being equal, dictated replacing the Cu with an Ag atom (Ag₅ model). Refinement produced a much lower R factor of 0.037 and a featureless ΔF map. The presence of Cu atoms in the elemental analysis and the improvement of the R factor indicate possible positional disorder in some Ag-atom positions. Refinement of the site-occupation factors (s.o.f.'s) of the metal atoms using the Ag₅ model confirms the presence of the positional disorder in the equatorial positions to the same extent, s.o.f.'s equal to 0.922 and 0.458 ($0.458 \times 2 = 0.916$) for atoms at general and special positions, respectively. Both Ag and Cu atoms were then included at each of the equatorial positions, given the same refinable displacement parameters and the sum of their s.o.f.'s tied to be equal to 1 for atoms at general positions and 0.5 for atoms at the special position. Final refinement produced $R = 0.032$ and s.o.f.'s of 0.821 (4) and 0.179 (4) for Ag and Cu atoms at general positions, respectively.

Data collection: XSCANS2.00a (Siemens, 1993). Cell refinement: XSCANS2.00a. Data reduction: XSCANS2.00a. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1991). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXL93.

We thank the Research Centre, College of Science, King Saud University, for providing crystallographic facilities.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: JZ1005). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Abu-Salah, O. M., Al-Ohaly, A. A. & Knobler, C. (1985). *J. Chem. Soc. Chem. Commun.* pp. 1502–1503.
- Abu-Salah, O. M., Al-Ohaly, A. A. & Mutter, Z. F. (1990). *J. Organomet. Chem.* **389**, 427–434.
- Corfield, P. W. & Shearer, H. M. M. (1966). *Acta Cryst.* **20**, 502–508.
- Kennard, O., Watson, D. G., Allen, F. H., Isaacs, N. W., Motherwell, W. D. S., Pettersen, R. C. & Town, W. G. (1972). *Molecular Structures and Dimensions*, Vol. A1, p. S2, Utrecht: NVA Oosthoek.
- Mazhar-Ul-Haque, Horne, W. & Abu-Salah, O. M. (1992). *J. Crystallogr. Spectrosc. Res.* **22**, 421–425.
- Sheldrick, G. M. (1991). *SHELXTL/PC*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

Siemens (1993). *XSCANS2.00a*. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Acta Cryst. (1995). **C51**, 1092–1094

Bis[hydrotris(1-pyrazolyl-N²)borato]zinc(II)

KOU NAKATA, SATOSHI KAWABATA AND
KAZUHIKO ICHIKAWA*

Division of Material Science, Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060, Japan

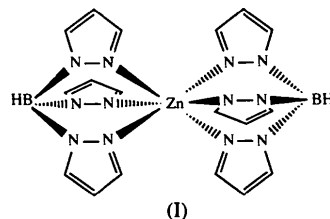
(Received 21 June 1994; accepted 29 November 1994)

Abstract

The crystal structure of the title compound, [Zn(C₉H₁₀BN₆)₂], has been determined. The Zn^{II} ion is coordinated by six N atoms, one from each of the six pyrazole rings. The coordination geometry about the Zn^{II} ion is distorted octahedral. The average Zn—N distance is 2.155 (11) Å and the average intraligand N—Zn—N bond angle is 85.6 (4)°, with average interligand N—Zn—N bond angles of 94 (2) and 177.2 (7)°.

Comment

A wide variety of [HB(pz)₃]⁻ (pz is pyrazolyl) and [HB(pz*)₃]⁻ (pz* is substituted pyrazolyl) complexes have been reported for transition metals and main group elements (Trofimenko, 1993). Recently, pyrazolylborate derivatives have played an important role in the synthesis of the model metalloenzyme complex, carbonic anhydrase (Loony, Han, McNeill & Parkin, 1993; Alsfasser, Ruf, Trofimenko & Vahrenkamp, 1993). Tetrahedral geometry is preferred for sterically bulky tris(pyrazolyl) derivatives. On the other hand, octahedral geometry is preferred for the less sterically hindered tris(pyrazolyl)borates. [HB(pz)₃]⁻ forms stable [M{HB(pz)₃}₂]-type complexes with divalent metal ions. Though the synthesis and characterization of [Zn{HB(pz)₃}₂], (I), have already been carried out (Trofimenko, 1967), the crystal structure of this complex has not yet been reported.



Figs. 1 and 2 show the molecular structure and the packing diagram of $[\text{Zn}\{\text{HB}(\text{pz})_3\}_2]$. The monomeric molecules show no intermolecular interaction. The shortest intermolecular distance (between atoms C14 and C63) is 3.50 Å. Each $[\text{HB}(\text{pz})_3]^-$ ligand is tridentate and the geometry around the Zn^{II} ion is distorted octahedral. The two $[\text{HB}(\text{pz})_3]^-$ ligands adopt staggered conformations. The Zn—N bond distances vary from 2.143 (2) to 2.175 (2) Å, with an average of 2.155 (11) Å (e.s.d.'s for average bond lengths and angles are calculated by r.m.s. methods). The 'octahedral' N—Zn—N bond angles range from 85.15 (8) to 96.99 (8)°. The average intraligand N—Zn—N bond angle is 85.6 (4)°; the average interligand angles are 94 (2) and 177.2 (7)° (involving opposite N atoms). The planes formed by the three N-donor atoms of each ligand (N11, N21, N31 and N41, N51, N61) are almost parallel [the dihedral angle between them is 0.88 (8)°]. The B...Zn distances are 3.208 (3) and 3.210 (3) Å, and the B...Zn...B angle is 178.4 (1)°. For the coordinated N atoms, the average intraligand N...N distance [2.928 (15) Å] is shorter than the average interligand N...N distance [3.16 (5) Å].

Crystal structures of $[M\{\text{HB}(\text{pz})_3\}_2]$ complexes have been reported for several divalent metal ions. For Ca^{II} , Mg^{II} , Co^{II} and Fe^{II} , the intraligand N—M—N bond angles are 79.2 (Sohrin *et al.*, 1993), 84.7 (Sohrin *et al.*, 1993), 85.5 (Churchill, Gold & Naw, 1970) and 88.2° (Oliver, Mullica, Hutchinson & Milligan, 1980), respectively. The degree of distortion from octahedral geometry (trigonal distortion) in $[\text{Zn}\{\text{HB}(\text{pz})_3\}_2]$ is similar to that in both $[\text{Co}\{\text{HB}(\text{pz})_3\}_2]$ and $[\text{Mg}\{\text{HB}(\text{pz})_3\}_2]$, while in the case of $[\text{Pb}\{\text{HB}(\text{pz})_3\}_2]$, the structure is capped octahedral because of the lone pair of electrons

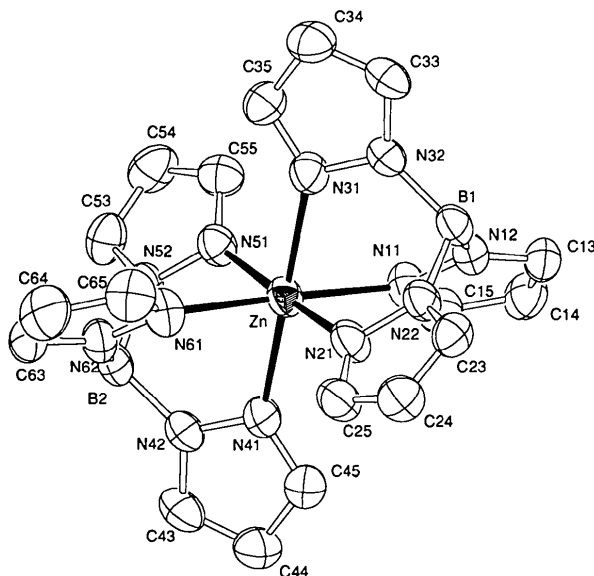


Fig. 1. ORTEPII (Johnson, 1976) drawing showing the atom-numbering scheme for $[\text{Zn}\{\text{HB}(\text{pz})_3\}_2]$. Displacement ellipsoids are depicted at the 50% probability level.

on the metal ion (Reger, Huff, Rheingold & Haggerty, 1992).

The geometry around the B atom is tetrahedral. The average B—N distance is 1.541 (3) Å. The average N—B—N and N—B—H angles are 108.9 (5) and 110.1 (17)°, respectively. The bond lengths and angles in the pyrazole rings are typical of the pyrazole molecule (Berthou, Elguero & Rérat, 1970).

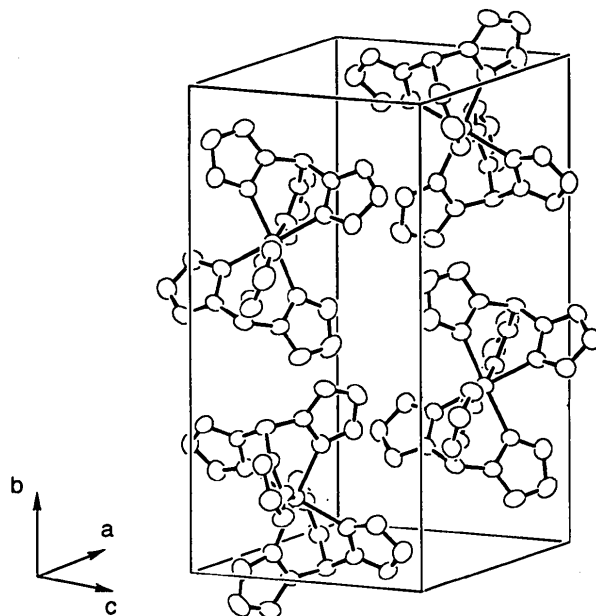


Fig. 2. Packing diagram of $[\text{Zn}\{\text{HB}(\text{pz})_3\}_2]$.

Experimental

The title compound, $[\text{Zn}\{\text{HB}(\text{pz})_3\}_2]$, was synthesized from $\text{Na}[\text{HB}(\text{pz})_3]$ and $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in aqueous solution according to the method of Trofimenko (1967). A single crystal suitable for X-ray crystallography was grown from a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution. The density D_m was measured by flotation in aqueous ZnCl_2 .

Crystal data

$[\text{Zn}(\text{C}_9\text{H}_{10}\text{BN}_6)_2]$
 $M_r = 491.45$
 Monoclinic
 $P2_1/n$
 $a = 13.342 (1) \text{ \AA}$
 $b = 17.709 (2) \text{ \AA}$
 $c = 9.723 (2) \text{ \AA}$
 $\beta = 97.23 (1)^\circ$
 $V = 2278.9 (5) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.43 \text{ Mg m}^{-3}$
 $D_m = 1.43 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 12.5\text{--}15^\circ$
 $\mu = 1.134 \text{ mm}^{-1}$
 Room temperature
 Hexagonal prism
 $0.7 \times 0.3 \times 0.3 \text{ mm}$
 Colorless

Data collection

Rigaku AFC-5R diffractometer

$R_{\text{int}} = 0.0175$
 $\theta_{\text{max}} = 30^\circ$

ω -2 θ scans $h = -19 \rightarrow 19$
 Absorption correction: $k = 0 \rightarrow 25$
 none $l = 0 \rightarrow 24$
 7347 measured reflections 3 standard reflections
 5287 independent reflections monitored every 150
 4887 observed reflections reflections
 $[|F| > 3\sigma|F|]$ intensity decay: <1%

Refinement

Refinement on F $R = 0.0467$ $wR = 0.0476$ $S = 1.79$

4887 reflections

379 parameters

All H-atom parameters refined

$$w = 1/[\sigma^2(|F_o|) + (0.015|F_o|)^2]$$

$$(\Delta/\sigma)_{\max} = 0.44$$

$$\Delta\rho_{\max} = 1.28 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.56 \text{ e } \text{Å}^{-3}$$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

N11—Zn—N21	85.93 (8)	N22—B1—N32	108.4 (2)
N11—Zn—N31	85.16 (7)	N42—B2—N52	109.3 (2)
N11—Zn—N41	93.06 (8)	N42—B2—N62	108.9 (2)
N11—Zn—N51	95.10 (8)	N52—B2—N62	108.3 (2)
N11—Zn—N61	178.01 (8)	Zn—N11—N12	118.42 (15)
N21—Zn—N31	85.69 (8)	Zn—N21—N22	117.97 (15)
N21—Zn—N41	96.99 (8)	Zn—N31—N32	118.03 (14)
N21—Zn—N51	176.83 (8)	Zn—N41—N42	117.68 (15)
N21—Zn—N61	93.40 (8)	Zn—N51—N52	117.79 (14)
N31—Zn—N41	176.69 (8)	Zn—N61—N62	118.36 (15)
N31—Zn—N51	91.41 (7)	N11—N12—B1	120.0 (2)
N31—Zn—N61	96.66 (8)	N21—N22—B1	120.5 (2)
N41—Zn—N51	85.96 (8)	N31—N32—B1	120.2 (2)
N41—Zn—N61	85.15 (8)	N41—N42—B2	120.9 (2)
N51—Zn—N61	85.67 (8)	N51—N52—B2	120.3 (2)
N12—B1—N22	108.6 (2)	N61—N62—B2	120.3 (2)
N12—B1—N32	109.7 (2)		

The structure was solved by Patterson methods and refined in the space group $P2_1/n$. The non-H atoms were refined anisotropically. The H atoms were introduced at theoretical positions and refined isotropically. The value of $(\Delta/\sigma)_{\max}$ is attributed to the shift in one of the parameters of the H25 atom. The position of H25 was shifted out of the pyrazole plane from the theoretical position because the environment around it was sterically crowded. Other H atoms did not show such shift.

Data collection: *MSC/AFC Data Collection Software* (Rigaku Corporation, 1988). Program used to solve structure: *UNICSIII* (Sakurai & Kobayashi, 1979). Molecular graphics: *ORTEPII* (Johnson, 1976). Computer: HITAC M880/210 at Hokkaido University.

The authors thank Dr K. Umakoshi and Professor Y. Sasaki (Hokkaido University) for experimental assistance and helpful discussion.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1006). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Alsasser, R., Ruf, M., Trofimenko, S. & Vahrenkamp, H. (1993). *Chem. Ber.* **126**, 703–710.
- Berthou, J., Elguero, J. & Rérat, C. (1970). *Acta Cryst.* **B26**, 1880–1881.
- Churchill, M. R., Gold, K. & Naw, C. E. Jr (1970). *Inorg. Chem.* **9**, 1597–1604.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Loony, A., Han, R., McNeill, K. & Parkin, G. (1993). *J. Am. Chem. Soc.* **115**, 4690–4697.
- Oliver, J. D., Mullica, D. F., Hutchinson, B. B. & Milligan, W. O. (1980). *Inorg. Chem.* **19**, 165–169.
- Reger, D. L., Huff, M. F., Rheingold, A. L. & Haggerty, B. S. (1992). *J. Am. Chem. Soc.* **114**, 579–584.
- Rigaku Corporation (1988). *MSC/AFC Data Collection Software*. Rigaku Corporation, Tokyo, Japan.
- Sakurai, T. & Kobayashi, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.
- Sohrin, Y., Kokusen, H., Kihara, S., Matsui, M., Kushi, Y. & Shiro, M. (1993). *J. Am. Chem. Soc.* **115**, 4128–4136.
- Trofimenko, S. (1967). *J. Am. Chem. Soc.* **89**, 3170–3177.
- Trofimenko, S. (1993). *Chem. Rev.* **93**, 943–980.

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

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
Zn	0.16124 (2)	0.14910 (1)	0.35436 (3)	3.2 (1)
N11	0.1997 (2)	0.2590 (1)	0.4386 (2)	3.8 (1)
N12	0.1347 (2)	0.3174 (1)	0.4031 (2)	3.5 (1)
N21	0.0101 (2)	0.1738 (1)	0.3956 (2)	3.9 (1)
N22	-0.0273 (1)	0.2443 (1)	0.3639 (2)	3.4 (1)
N31	0.1205 (1)	0.2081 (1)	0.1607 (2)	3.6 (1)
N32	0.0663 (1)	0.2735 (1)	0.1632 (2)	3.3 (1)
N41	0.2105 (2)	0.0930 (1)	0.5475 (2)	3.8 (1)
N42	0.2654 (1)	0.0283 (1)	0.5428 (2)	3.4 (1)
N51	0.3112 (1)	0.1247 (1)	0.3005 (2)	3.5 (1)
N52	0.3505 (1)	0.0547 (1)	0.3315 (2)	3.5 (1)
N61	0.1222 (1)	0.0382 (1)	0.2774 (2)	3.8 (1)
N62	0.1900 (2)	-0.0191 (1)	0.3095 (2)	3.5 (1)
C13	0.1672 (2)	0.3789 (1)	0.4771 (3)	4.1 (1)
C14	0.2537 (2)	0.3611 (2)	0.5619 (3)	4.6 (1)
C15	0.2707 (2)	0.2859 (2)	0.5340 (3)	4.2 (1)
C23	-0.1229 (2)	0.2483 (1)	0.3922 (3)	3.7 (1)
C24	-0.1494 (2)	0.1801 (2)	0.4432 (3)	4.4 (1)
C25	-0.0642 (2)	0.1361 (1)	0.4435 (3)	4.3 (1)
C33	0.0440 (2)	0.2995 (1)	0.0333 (3)	3.8 (1)
C34	0.0844 (2)	0.2515 (2)	-0.0550 (3)	4.4 (1)
C35	0.1315 (2)	0.1956 (2)	0.0292 (3)	3.9 (1)
C43	0.2872 (2)	0.0011 (1)	0.6718 (3)	4.2 (1)
C44	0.2463 (3)	0.0473 (2)	0.7621 (3)	5.2 (1)
C45	0.1993 (2)	0.1039 (2)	0.6790 (3)	4.5 (1)
C53	0.4362 (2)	0.0465 (2)	0.2745 (3)	4.4 (1)
C54	0.4543 (2)	0.1117 (2)	0.2069 (3)	4.9 (1)
C55	0.3744 (2)	0.1582 (2)	0.2255 (3)	4.0 (1)
C63	0.1547 (2)	-0.0823 (1)	0.2439 (3)	4.4 (1)
C64	0.0644 (2)	-0.0672 (2)	0.1695 (3)	5.6 (1)
C65	0.0467 (2)	0.0081 (2)	0.1927 (3)	4.8 (1)
B1	0.0380 (2)	0.3041 (2)	0.3012 (3)	3.5 (1)
B2	0.2897 (2)	-0.0040 (2)	0.4033 (3)	3.6 (1)

Table 2. Selected geometric parameters (Å , $^\circ$)

Zn—N11	2.148 (2)	N51—N52	1.365 (3)
Zn—N21	2.150 (2)	N61—N62	1.368 (3)
Zn—N31	2.162 (2)	N12—B1	1.543 (4)
Zn—N41	2.152 (2)	N22—B1	1.544 (3)
Zn—N51	2.175 (2)	N32—B1	1.537 (3)
Zn—N61	2.143 (2)	N42—B2	1.543 (4)
N11—N12	1.366 (3)	N52—B2	1.539 (4)
N21—N22	1.365 (3)	N62—B2	1.538 (4)
N31—N32	1.366 (3)	Zn—B1	3.208 (3)
N41—N42	1.364 (3)	Zn—B2	3.210 (3)