Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

A tetragonal polymorph of bis[hydrotris(pyrazol-1-yl)borato]iron(II)

Zhong-Hai Ni,* Guo-Ling Li, Rui Ma and Jing Nie

School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, Jiangsu Province, People's Republic of China
Correspondence e-mail: nizhonghai@cumt.edu.cn

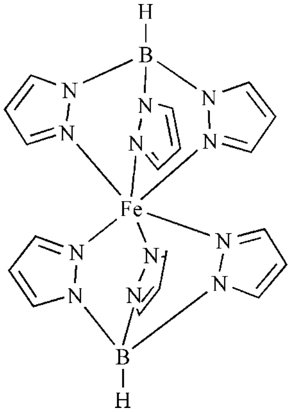
Received 22 June 2011; accepted 30 June 2011

Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.003 Å; R factor = 0.037; wR factor = 0.123; data-to-parameter ratio = 12.6.

The title compound, $[Fe(C_9H_{10}BN_6)_2]$, is a polymorph of a compound reported previously [Oliver *et al.* (1980). *Inorg. Chem.* **19**, 165–168]. In the previous report, the compound crystallized in the monoclinic space group $P2_1/c$ (Z = 4), whereas the crystal symmetry of the compound reported here is tetragonal ($P4_2/ncm$, Z = 4). The molecular structure is comprised of two hydrotris(1-pyrazolyl)borate ligands (Tp^-) and a central Fe^{II} ion, which is coordinated by six pyrazole N atoms from two two Tp^- ligands, yielding a distorted bipyramidal FeN_6 geometry. The complete molecule exhibits symmetry $2/m$.

Related literature

For the crystal structure of the other polymorph measured at room temperature, see: Oliver *et al.* (1980). For iron(II) complexes with the Tp^- derivative ligands, see: Janiak *et al.* (2000); Reger *et al.* (2005).



Experimental

Crystal data

$[Fe(C_9H_{10}BN_6)_2]$
M_r = 481.93
Tetragonal, $P4_2/ncm$
a = 17.017 (3) Å
c = 7.4099 (15) Å
V = 2145.7 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.74 mm^{-1}
T = 123 K
0.20 × 0.15 × 0.12 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.867, T_{max} = 0.916
14091 measured reflections
1099 independent reflections
1095 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.123
S = 0.95
1099 reflections
87 parameters
H-atom parameters not refined
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Sheldrick, 1998); software used to prepare material for publication: *XP*.

This work was supported by the Fundamental Research Funds for the Central Universities (China University of Mining and Technology). The authors thank Professors Hui-Zhong Kou and Seik Weng Ng for helpful comments and assistance in the preparation of this paper.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG5058).

References

Bruker (2001). *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2004). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Janiak, C., Temizdemir, S., Dechert, S., Deck, W., Girgsdies, F., Heinze, J., Kolm, M., Scharmann, T. G. & Zipffel, O. M. (2000). *Eur. J. Inorg. Chem.* pp. 1229–1236.
Oliver, J. D., Mullica, D. F., Hutchinson, B. B. & Milligan, W. O. (1980). *Inorg. Chem.* **19**, 165–168.
Reger, D. L., Gardinier, J. R., Smith, M. D., Shahin, A. M., Long, G. J., Rebbouh, L. & Grandjean, F. (2005). *Inorg. Chem.* **44**, 1852–1856.
Sheldrick, G. M. (1998). *XP*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2011). E**67**, m1033 [**doi:10.1107/S1600536811025839**]

A tetragonal polymorph of bis[hydrotris(pyrazol-1-yl)borato]iron(II)

Z.-H. Ni, G.-L. Li, R. Ma and J. Nie

Comment

Recently, hydro-tris(1-pyrazolyl)-borate (Tp^-)and its derivatives have been employed as tridentate ligands to assembly molecular functional materials such as cyanide-bridged magnetic complexes, spin cross-over compounds and optic materials. In these cases, some mononuclear iron(II) complexes with two such tridendate ligands have been synthesized and crystal structures characterized (Janiak *et al.*, 2000; Reger *et al.*, 2005). The crystal structure of the title compound has been reported previously (Oliver *et al.*, 1980) which was measured at room temperature and crystallized in monoclinic space group of $P2_1/c$ ($Z = 4$). Recently, we synthesized this compound and measured its crystal structure at temperature 123 K. The result indicated that the crystal structure of the compound is significantly from the previous report. Herein, we report the crystal structure of the title compound $[Fe^{II}(C_9H_{10}N_6B)_2]$ (I).

The title compound in this paper crystallizes in a tetragonal space group $P4_2$/ncm, suggesting there is a fourfold rotation symmetry axis in the unit cell. In the molecular structure of the title compound, there is a pseudo C_3 rotation axis. The geometry and labeling scheme for the crystal structure of the title complex are depicted in Figure 1. The molecular structure of title compound in this work comprises of two Tp^- ligands and one central iron(II) ion. In the molecular structure, the cental metal iron(II) ion is coordinated by six pyrazole nitrogen atoms from the same two Tp^- ligands, yielding a distorted bipyramidal FeN_6 geometry.

The Fe—N bond length is 1.975 (2)Å for Fe1—N2 and 1.983 (2)Å for Fe1—N4, respectively. which are simiar to those in the polymorph of the title compound reported previously at room temperature (Oliver *et al.*, 1980). The N—Fe—N bond angle is 89.05 (18)° for N2—Fe1—N4 and 88.33 (18)° for N2—Fe1—N2[+*y*, +*x*, +*z*.], respectively. These Fe—N bond lengthes suggest that the iron(II) center of the title compound is low spin state whether at low temperature or at room temperature (Oliver *et al.*, 1980).

Experimental

The title complex was prepared as following: methanol solution (10 ml) of $[Fe^{II}(BF_4)_2].4H_2O$ (30 mg, 0.1 mmol) was added slowly into a MeOH and aqueous solution (20 ml, water and methanol with $v/v = 1/1$) containing the ligand KTp (50.4 mg, 0.2 mmol). Then, the mixture was carefully filtered and the resulting solution was kept at room temperature for about two days, producing block brown crystals of (I) with yield 50%.

Refinement

The coordinates of the H atom bound to boron atom was found from difference Fourier maps and refined freely. H atoms bound to C atoms were placed using the HFIX commands in *SHELXL-97*, with C—H distances of 0.93 Å. All H atoms were allowed for as riding atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

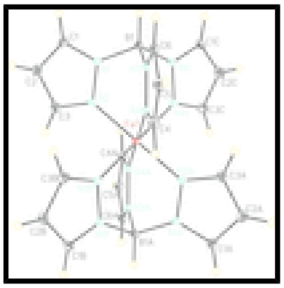


Fig. 1. A view of (I) with the unique atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. [symmetry code: (A) -*x*, -*y*, -*z*; (B) -*y*, -*x*, -*z*; (C) +*y*, +*x*, +*z*.]

bis[hydrotris(pyrazol-1-yl)borato]iron(II)

Crystal data

$[Fe(C_9H_{10}BN_6)_2]$

$M_r = 481.93$

Tetragonal, $P4_2/ncm$

Hall symbol: -P 4ac 2ac

$a = 17.017$ (3) Å

$c = 7.4099$ (15) Å

$V = 2145.7$ (7) Å^3

$Z = 4$

$F(000) = 992$

$D_x = 1.492$ Mg m^{-3}

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 1210 reflections

θ = 2.4–27.1°

μ = 0.74 mm^{-1}

$T = 123$ K

Block, brown

0.2 × 0.15 × 0.12 mm

Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

graphite

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)

$T_{min} = 0.867$, $T_{max} = 0.916$

14091 measured reflections

1099 independent reflections

1095 reflections with $I > 2\sigma(I)$

$R_{int} = 0.034$

$\theta_{max} = 26.0°$, $\theta_{min} = 3.4°$

$h = -20 \rightarrow 20$

$k = -20 \rightarrow 16$

$l = -9 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.123$

$S = 0.95$

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0908P)^2 + 2.7074P]$
where $P = (F_o^2 + 2F_c^2)/3$

1099 reflections

87 parameters

0 restraints

$(\Delta/\sigma)_{\mathrm{max}} < 0.001$

$\Delta\rho_{\mathrm{max}} = 0.43$ e Å^{-3}

$\Delta\rho_{\mathrm{min}} = -0.39$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Fe1	0	0	0	0.0125 (3)
B1	0.11871 (13)	0.11871 (13)	0.1589 (4)	0.0150 (6)
H1A	0.1588 (14)	0.1588 (14)	0.211 (4)	0.013 (7)*
C1	0.19598 (12)	0.00348 (11)	0.3210 (3)	0.0173 (5)
H1	0.2365	0.0317	0.3749	0.021*
C2	0.18477 (12)	−0.07653 (13)	0.3322 (3)	0.0218 (5)
H2	0.2154	−0.1127	0.3947	0.026*
C3	0.11737 (12)	−0.09163 (12)	0.2293 (3)	0.0201 (5)
H3	0.0954	−0.1411	0.2117	0.024*
C4	0.08225 (9)	0.08225 (9)	−0.3162 (3)	0.0176 (6)
H4	0.0562	0.0562	−0.4090	0.021*
C5	0.13997 (9)	0.13996 (9)	−0.3405 (3)	0.0196 (6)
H5	0.1594	0.1594	−0.4491	0.024*
C6	0.16160 (12)	0.16160 (12)	−0.1690 (4)	0.0179 (6)
H6	0.1992	0.1992	−0.1401	0.021*
N1	0.13791 (9)	0.03379 (9)	0.2180 (2)	0.0157 (4)
N2	0.08928 (10)	−0.02509 (10)	0.1603 (2)	0.0162 (4)
N3	0.11954 (9)	0.11954 (9)	−0.0499 (3)	0.0148 (5)
N4	0.07002 (9)	0.07002 (9)	−0.1405 (3)	0.0152 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0106 (3)	0.0106 (3)	0.0163 (4)	−0.00276 (17)	−0.00002 (13)	−0.00002 (13)
B1	0.0120 (9)	0.0120 (9)	0.0212 (15)	−0.0015 (11)	−0.0007 (8)	−0.0007 (8)
C1	0.0121 (10)	0.0198 (11)	0.0201 (10)	−0.0007 (7)	−0.0028 (8)	0.0015 (7)
C2	0.0177 (10)	0.0192 (10)	0.0283 (11)	0.0014 (8)	−0.0013 (8)	0.0071 (8)
C3	0.0198 (10)	0.0135 (9)	0.0270 (11)	−0.0020 (7)	0.0006 (8)	0.0030 (8)
C4	0.0183 (9)	0.0183 (9)	0.0162 (13)	−0.0024 (11)	−0.0005 (7)	−0.0005 (7)

C5	0.0194 (9)	0.0194 (9)	0.0201 (14)	−0.0011 (11)	0.0032 (8)	0.0032 (8)
C6	0.0136 (8)	0.0136 (8)	0.0266 (15)	−0.0008 (10)	0.0027 (8)	0.0027 (8)
N1	0.0144 (8)	0.0131 (9)	0.0197 (8)	−0.0031 (6)	−0.0012 (6)	−0.0007 (6)
N2	0.0144 (8)	0.0128 (8)	0.0216 (8)	−0.0034 (6)	−0.0004 (6)	−0.0009 (6)
N3	0.0111 (7)	0.0111 (7)	0.0223 (12)	−0.0020 (8)	0.0001 (6)	0.0001 (6)
N4	0.0134 (7)	0.0134 (7)	0.0190 (11)	−0.0024 (9)	−0.0006 (6)	−0.0006 (6)

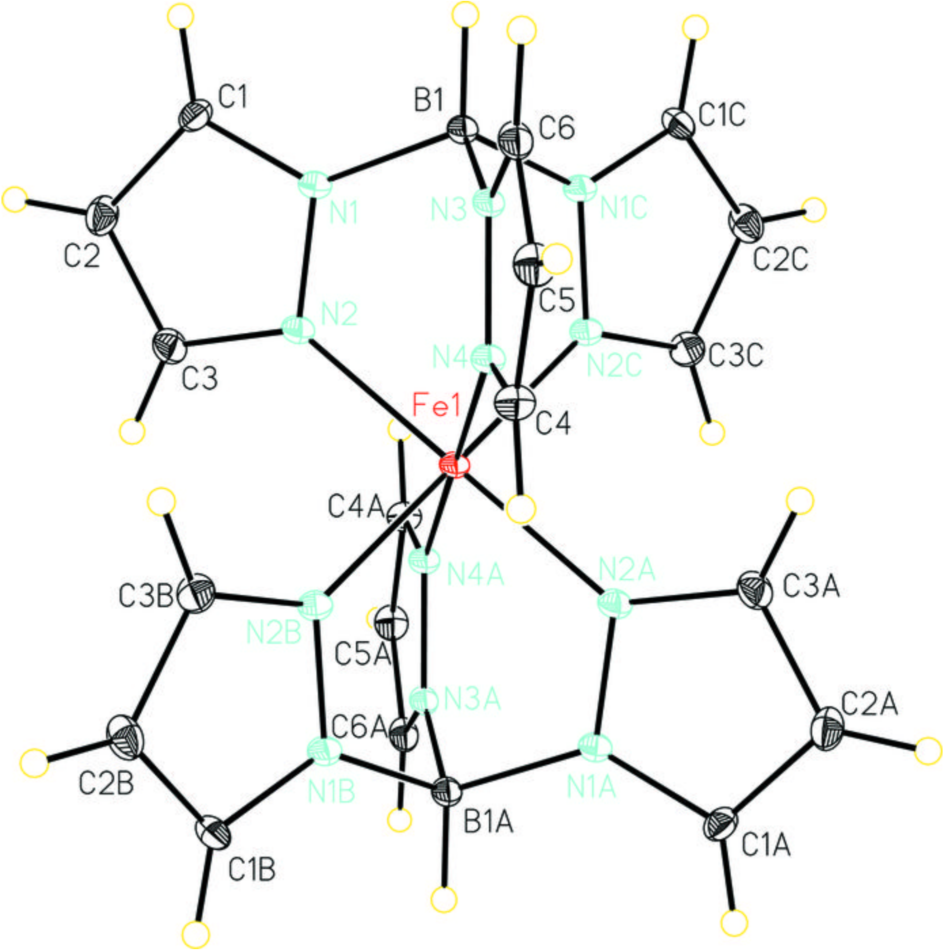
Geometric parameters (Å, °)

Fe1—N2$^{\mathrm{i}}$	1.9751 (17)	C2—C3	1.401 (3)
Fe1—N2$^{\mathrm{ii}}$	1.9751 (17)	C2—H2	0.9300
Fe1—N2	1.9751 (17)	C3—N2	1.331 (3)
Fe1—N2$^{\mathrm{iii}}$	1.9751 (17)	C3—H3	0.9300
Fe1—N4$^{\mathrm{iii}}$	1.981 (2)	C4—N4	1.335 (3)
Fe1—N4	1.981 (2)	C4—C5	1.4005
B1—N1$^{\mathrm{ii}}$	1.545 (2)	C4—H4	0.9300
B1—N1	1.545 (2)	C5—C6	1.374 (4)
B1—N3	1.547 (4)	C5—H5	0.9300
B1—H1A	1.04 (3)	C6—N3	1.343 (4)
C1—N1	1.351 (3)	C6—H6	0.9300
C1—C2	1.377 (3)	N1—N2	1.368 (2)
C1—H1	0.9300	N3—N4	1.368 (3)
N2$^{\mathrm{i}}$—Fe1—N2$^{\mathrm{ii}}$	180.00 (6)	C3—C2—H2	127.4
N2$^{\mathrm{i}}$—Fe1—N2	91.67 (10)	N2—C3—C2	110.30 (18)
N2$^{\mathrm{ii}}$—Fe1—N2	88.33 (10)	N2—C3—H3	124.9
N2$^{\mathrm{i}}$—Fe1—N2$^{\mathrm{iii}}$	88.33 (10)	C2—C3—H3	124.9
N2$^{\mathrm{ii}}$—Fe1—N2$^{\mathrm{iii}}$	91.67 (10)	N4—C4—C5	110.13 (13)
N2—Fe1—N2$^{\mathrm{iii}}$	180.00 (14)	N4—C4—H4	124.9
N2$^{\mathrm{i}}$—Fe1—N4$^{\mathrm{iii}}$	89.05 (7)	C5—C4—H4	124.9
N2$^{\mathrm{ii}}$—Fe1—N4$^{\mathrm{iii}}$	90.95 (7)	C6—C5—C4	104.89 (14)
N2—Fe1—N4$^{\mathrm{iii}}$	90.95 (7)	C6—C5—H5	127.6
N2$^{\mathrm{iii}}$—Fe1—N4$^{\mathrm{iii}}$	89.05 (7)	C4—C5—H5	127.6
N2$^{\mathrm{i}}$—Fe1—N4	90.95 (7)	N3—C6—C5	108.8 (2)
N2$^{\mathrm{ii}}$—Fe1—N4	89.05 (7)	N3—C6—H6	125.6
N2—Fe1—N4	89.05 (7)	C5—C6—H6	125.6
N2$^{\mathrm{iii}}$—Fe1—N4	90.95 (7)	C1—N1—N2	109.85 (16)
N4$^{\mathrm{iii}}$—Fe1—N4	180.00 (18)	C1—N1—B1	132.23 (18)
N1$^{\mathrm{ii}}$—B1—N1	108.4 (2)	N2—N1—B1	117.93 (17)
N1$^{\mathrm{ii}}$—B1—N3	106.87 (15)	C3—N2—N1	106.59 (16)
N1—B1—N3	106.87 (15)	C3—N2—Fe1	133.71 (14)
N1$^{\mathrm{ii}}$—B1—H1A	111.6 (9)	N1—N2—Fe1	119.67 (13)
N1—B1—H1A	111.6 (9)	C6—N3—N4	109.5 (2)
N3—B1—H1A	111.2 (17)	C6—N3—B1	131.8 (2)
N1—C1—C2	108.08 (18)	N4—N3—B1	118.6 (2)

N1—C1—H1	126.0	C4—N4—N3	106.6 (2)
C2—C1—H1	126.0	C4—N4—Fe1	134.45 (17)
C1—C2—C3	105.17 (18)	N3—N4—Fe1	118.91 (18)
C1—C2—H2	127.4		
N1—C1—C2—C3	0.4 (2)	N4$^{\text{iii}}$—Fe1—N2—N1	−136.67 (14)
C1—C2—C3—N2	−0.2 (2)	N4—Fe1—N2—N1	43.33 (14)
N4—C4—C5—C6	0.0	C5—C6—N3—N4	0.0
C4—C5—C6—N3	0.0	C5—C6—N3—B1	180.0
C2—C1—N1—N2	−0.6 (2)	N1$^{\text{ii}}$—B1—N3—C6	122.08 (15)
C2—C1—N1—B1	179.4 (2)	N1—B1—N3—C6	−122.08 (15)
N1$^{\text{ii}}$—B1—N1—C1	−124.0 (2)	N1$^{\text{ii}}$—B1—N3—N4	−57.92 (15)
N3—B1—N1—C1	121.1 (2)	N1—B1—N3—N4	57.92 (15)
N1$^{\text{ii}}$—B1—N1—N2	55.9 (3)	C5—C4—N4—N3	0.0
N3—B1—N1—N2	−58.9 (2)	C5—C4—N4—Fe1	−180.0
C2—C3—N2—N1	−0.2 (2)	C6—N3—N4—C4	0.0
C2—C3—N2—Fe1	178.11 (14)	B1—N3—N4—C4	180.0
C1—N1—N2—C3	0.4 (2)	C6—N3—N4—Fe1	180.0
B1—N1—N2—C3	−179.50 (18)	B1—N3—N4—Fe1	0.0
C1—N1—N2—Fe1	−178.13 (13)	N2$^{\text{i}}$—Fe1—N4—C4	44.17 (5)
B1—N1—N2—Fe1	1.9 (2)	N2$^{\text{ii}}$—Fe1—N4—C4	−135.83 (5)
N2$^{\text{i}}$—Fe1—N2—C3	−43.85 (17)	N2—Fe1—N4—C4	135.83 (5)
N2$^{\text{ii}}$—Fe1—N2—C3	136.15 (17)	N2$^{\text{iii}}$—Fe1—N4—C4	−44.17 (5)
N2$^{\text{iii}}$—Fe1—N2—C3	39 (32)	N4$^{\text{iii}}$—Fe1—N4—C4	0(100)
N4$^{\text{iii}}$—Fe1—N2—C3	45.2 (2)	N2$^{\text{i}}$—Fe1—N4—N3	−135.83 (5)
N4—Fe1—N2—C3	−134.8 (2)	N2$^{\text{ii}}$—Fe1—N4—N3	44.17 (5)
N2$^{\text{i}}$—Fe1—N2—N1	134.26 (16)	N2—Fe1—N4—N3	−44.17 (5)
N2$^{\text{ii}}$—Fe1—N2—N1	−45.74 (16)	N2$^{\text{iii}}$—Fe1—N4—N3	135.83 (5)
N2$^{\text{iii}}$—Fe1—N2—N1	−143 (32)	N4$^{\text{iii}}$—Fe1—N4—N3	180.00 (3)

Symmetry codes: (i) −*y*, −*x*, −*z*; (ii) *y*, *x*, *z*; (iii) −*x*, −*y*, −*z*.

Fig. 1


C1
B1
C6
C1C
C2
N1
N3
N1C
C2C
C5
N2
N4
N2C
C3C
C3
Fe1
C4
C4A
N4A
N2A
C3A
C3B
N2B
C5A
N3A
C2A
C6A
N1B
N1A
C2B
B1A
C1A
C1B