

Structure of Hexakis(pyrazole)nickel(II) Bis(tetrafluoroborate), $[\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_6](\text{BF}_4)_2$

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Abstract. $M_r = 640.82$, trigonal, $P\bar{3}$, $a = 9.810$ (2), $c = 7.879$ (1) Å, $V = 656.6$ (3) Å³, $Z = 1$, $D_x = 1.61$, $D_m = 1.59$ (2) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 8.33$ cm⁻¹, final $R = 0.059$ for 812 significant [$I > 2\sigma(I)$] reflexions. The Ni²⁺ ion lies at the center of a nearly regular octahedron of coordinating N atoms. The complex cation formed by the coordination of six planar pyrazole molecules to the Ni²⁺ ion has point symmetry $\bar{3}$. Hydrogen bonding between the N–H group of the pyrazole ring and the anions is weak.

Introduction. Pyrazole, a five-membered aromatic heterocycle containing two vicinal N atoms, forms a variety of complexes with transition-metal ions. Metal-to-ligand bond formation takes place *via* the pyridine-type N atom. Infrared spectra of pyrazole compounds with transition-metal chlorides, bromides and nitrates show that in these complexes the H atom on the pyrrole-type N forms hydrogen bonds with the anions. These findings have been confirmed by the X-ray structural analysis of Ni(pyrazole)₄Cl₂ (Reimann, Mighell & Mauer, 1967), Ni(pyrazole)₄Br₂ (Mighell, Reimann & Santoro, 1969), and [Ni(pyrazole)₆](NO₃)₂ (Reimann, Santoro & Mighell, 1970). In the hexakis(pyrazole) compounds of transition-metal tetrafluoroborates and perchlorates weak hydrogen bonding to the anions has been proposed also to occur on the basis of infrared data (Reedijk, 1969), although generally these anions have very little tendency to take part in hydrogen-bond formation with the ligands. In order to solve this discrepancy and to contribute to the important field of the coordination chemistry of pyrazole and its derivatives the crystal structure analysis of [Ni(pyrazole)₆](BF₄)₂ has been undertaken. In addition, it cannot be predicted whether this compound has trigonal symmetry or not, as both [Ni(pyrazole)₆](NO₃)₂ (Reimann *et al.*, 1970) and [Ni(imidazole)₆](NO₃)₂ (Santoro, Mighell, Zocchi & Reimann, 1969) have trigonal symmetry, while [Ni(imidazole)₆](BF₄)₂ is not trigonal, having space group $P2_1/n$ (van Ingen-Schenau, 1975).

Experimental. D_m from flotation method, chloroform–dibromoethane; blue elongated prisms grown from ethanol at room temperature (Reedijk, 1969); $0.42 \times 0.25 \times 0.25$ mm; Enraf–Nonius CAD-4 four-circle diffractometer; graphite-monochromatized Mo $K\alpha$; cell constants from setting angles of 24 reflections; corrections taken for Lorentz and polarization effects; no absorption correction performed as transmission coefficients varied from 0.88 to 0.93; room temperature; $\theta_{\text{max}} = 27^\circ$; $h = -12$ to 12, $k = -12$ to 12, $l = -10$ to 10; 3336 measured reflections; 956 independent reflections; direct methods; $S = 3.964$; $w = 1/\sigma^2(F)$; $R_w = 0.058$; $\dagger F(000) = 326.4$; scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); the Leiden University Computers IBM 370/158 and Amdahl V7B with programs written or modified by Mrs E. W. Rutten-Keulemans and R. A. G. de Graaff; H atoms with fixed isotropic thermal factor of 4.0 Å² placed at distances of 0.90 Å from the parent atoms.

Discussion. Positional parameters and isotropic B values for the non-hydrogen atoms are listed in Table 1; the corresponding labelling of the atoms is given in Fig. 1.

[†] Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38172 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ($\times 10^4$) and isotropic thermal parameters (Å²) for [Ni(pyrazole)₆](BF₄)₂

	$B_{\text{iso}} = \frac{1}{3} \pi^2 \text{trace } \bar{U}$			
	x	y	z	B_{iso}
Ni	0	0	0	3.36
N(1)	1987 (4)	1330 (4)	1525 (4)	4.14
N(2)	2876 (5)	2859 (5)	1514 (5)	5.86
C(3)	4016 (6)	3385 (7)	2711 (7)	6.80
C(4)	3874 (6)	2182 (7)	3527 (6)	5.85
C(5)	2579 (6)	914 (6)	2825 (6)	5.35
B	3333	6667	1592 (16)	6.64
F(1)	3333	6667	3247 (8)	11.53
F(2)	3267 (8)	7890 (7)	1051 (7)	15.10

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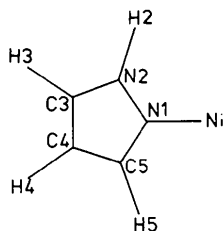


Fig. 1. Atomic numbering of the ligand in $[\text{Ni}(\text{pyrazole})_6](\text{BF}_4)_2$.

The crystal structure of $[\text{Ni}(\text{pyrazole})_6](\text{BF}_4)_2$ viewed along the c axis is shown in Fig. 2. The special position $\bar{3}$ is occupied by the Ni^{2+} ion at (0,0,0). The B atoms and two of the F atoms lie on the special positions 3 at $(\frac{1}{3}, \frac{2}{3}, z)$ and $(\frac{2}{3}, \frac{1}{3}, z)$. Each pyrazole molecule coordinates through the pyridine N, forming a nearly regular octahedron around the Ni^{2+} ion. $\text{N}(1)-\text{Ni}-\text{N}(1')$ angles deviate only slightly from 90° , i.e. $89.5(1)$ and $90.5(1)^\circ$. Relevant bond distances and angles are given in Table 2. The $\text{Ni}-\text{N}(1)$ distance is comparable to those found in related structures (Reimann *et al.*, 1970). The $\text{N}-\text{H}$ group is engaged in weak hydrogen bonding to the anion: the distance of this group to the nearest F atom is: $\text{N}(2)-\text{F}(2) = 2.942(8)$ Å. The lower $\text{N}-\text{H}$

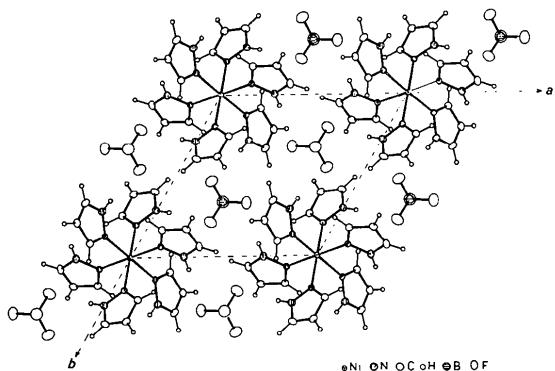


Fig. 2. ORTEP projection (Johnson, 1965) of $[\text{Ni}(\text{pyrazole})_6](\text{BF}_4)_2$ viewed along the c axis.

Table 2. Bond distances (Å) and bond angles ($^\circ$) for $[\text{Ni}(\text{pyrazole})_6](\text{BF}_4)_2$

Ni—N(1)	2.098 (3)	Ni—N(1)—N(2)	126.2 (3)
N(1)—N(2)	1.305 (5)	Ni—N(1)—C(5)	131.2 (3)
N(2)—C(3)	1.353 (6)	C(5)—N(1)—N(2)	102.3 (4)
C(3)—C(4)	1.294 (8)	N(1)—N(2)—C(3)	112.6 (5)
C(4)—C(5)	1.377 (7)	N(2)—C(3)—C(4)	108.2 (5)
C(5)—N(1)	1.338 (5)	C(3)—C(4)—C(5)	104.4 (4)
F(1)—B	1.304 (13)	C(4)—C(5)—N(1)	112.4 (5)
F(2)—B	1.305 (6)	F(1)—B—F(2)	109.1 (6)
		F(2)—B—F(2')	115.2 (3)

stretching frequencies and the higher $\text{N}-\text{H}$ bending frequencies of pyrazole in its transition-metal fluoroborates compared with gaseous pyrazole (Reedijk, 1969) are therefore due to relatively weak hydrogen bonding to the anions. The amount of lowering of the $\text{N}-\text{H}$ stretching frequency and the actual $\text{N}-\text{H}\cdots\text{F}$ distance fit fairly well the relationship developed by Bellamy & Owen (1969).

The pyrazole ring is almost planar, the largest distance to the best-fitted plane being $0.017(3)$ Å. The $\text{N}(1)-\text{N}(2)$ bond and the $\text{C}(3)-\text{C}(4)$ bond are shorter than in the compounds $[\text{Ni}(\text{pyrazole})_6](\text{NO}_3)_2$ (Reimann *et al.*, 1970), $\text{Ni}(\text{pyrazole})_4\text{Cl}_2$ (Reimann *et al.*, 1967), and $\text{Ni}(\text{pyrazole})_4\text{Br}_2$ (Mighell *et al.*, 1969), possibly as a consequence of the much stronger hydrogen bonding to the anions in the latter three compounds compared with our compound. The F atoms lie around the B atom in a tetrahedron which is slightly distorted trigonally: The $\text{B}-\text{F}$ distances are equal, but the $\text{F}-\text{B}-\text{F}$ angles are different. This distortion is too small for detection by infrared measurements, as no splitting of the tetrahedral $\text{B}-\text{F}$ vibrations occurred (Reedijk, 1969). The large temperature parameters of the F atoms (due perhaps to some disorder) are not unusual in hexasolvated coordination compounds in which the anions are only very weakly bonded to the cations.

X-ray powder diagrams have shown (Reedijk, 1969) that the pyrazole compounds of Mg^{II} and Ni^{II} perchlorate and of Mn^{II} , Fe^{II} , Co^{II} , Zn^{II} , and Cd^{II} perchlorate and tetrafluoroborate are isomorphous with $[\text{Ni}(\text{pyrazole})_6](\text{BF}_4)_2$.

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