International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Kaiser, J., Brauer, G. & Schroder, F. A. (1974). *J. Chem. Soc. Dalton Trans.* pp. 1490–1493.

Kobayashi, K., Sakurai, T., Hasegawa, A., Tsuboyama, S. & Tsuboyama, K. (1982). *Acta Cryst.* B**38**, 1154–1158.

Marsh, W. C. & Trotter, J. (1971). *J. Chem. Soc. A*, pp. 1482–1486.

Sakurai, T. & Kobayashi, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77 (in Japanese).

Sakurai, T., Kobayashi, K., Hasegawa, A., Tsuboyama, S. & Tsuboyama, K. (1982). *Acta Cryst.* B**38**, 107–111.

Tsuboyama, S., Tsuboyama, K., Sakurai, T., Kobayashi, K., Kajikawa, Y. & Ishizu, K. (1982). In preparation.

Acta Cryst. (1983). C**39**, 337–339

The Structure of Hexakis(2-methyltetrazole)nickel(II) Bis(tetrafluoroborate), $[\mathrm{Ni}(\mathrm{C_2H_4N_4})_6](\mathrm{BF_4})_2$*

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(*Received* 17 *May* 1982; *accepted* 9 *November* 1982)

Abstract. $\mathrm{C_{12}H_{24}N_{24}Ni.2BF_4}$, $M_r = 736{\cdot}80$, $P\bar{3}$, $a = b = 11{\cdot}311\ (3)$, $c = 7{\cdot}125\ (4)$ Å, $V = 789{\cdot}4$ Å^3, $Z = 1$, $D_c = 1{\cdot}55$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 7{\cdot}09$ cm^{-1}, $F(000) = 374{\cdot}4$, $R = 0{\cdot}039$ ($wR = 0{\cdot}040$) for 772 independent significant reflections. The compound consists of monomeric units in which only the N(4) atom appears to be coordinating. Octahedral geometry is observed. The two $\mathrm{BF_4^-}$ ions in the unit cell are found to be disordered. Two possible orientations exist with occupancy factors of 0·57 and 0·43.

Introduction. The coordination chemistry of tetrazole (HTz) and its derivatives has been the subject of many investigations. Nevertheless, little is known about the coordination site of the tetrazole ring and the nature of the metal–tetrazole interaction.

Tetrazole and 5-substituted tetrazoles form salts with a wide range of transition-metal ions (Holm & Donnelly, 1966; Garber, Sims & Brubaker, 1968; Mihina & Herbst, 1950; Daugherty & Brubaker, 1961 *a, b*; Jonassen, Terry & Harris, 1963; Harris, Herber, Jonassen & Wertheim, 1963; Harris, Jonassen & Archer, 1965; Labine & Brubaker, 1971; Franke & Groenveld, 1980*a,b*). Most of these complexes are considered to be polynuclear.

Transition-metal complexes of 1-substituted tetrazoles (1RTz) have also been reported (Gilbert & Brubaker, 1963; Biefield & Gilbert, 1971; Franke & Groeneveld, 1981). On 2-substituted tetrazoles (2RTz), however, very little is known with regard to coordinating aspects with transition-metal ions. Comparison with 1-substituted tetrazoles (Franke & Groeneveld, 1981; Ostrovskii, Panina, Koldobskii, Gidaspov & Shirobokov, 1979) lead to the expectation that 2-alkytetrazoles (van den Heuvel, Franke, Everstijn & Zuur, 1983) would be very strong monodentate ligands (Franke, 1982).

Ligand-field spectra showed a regular octahedral environment for the metal ions in this structure (van den Heuvel, Franke, Everstijn & Zuur, 1983).

In order to determine the exact coordination site, which could be N(1), N(3) or N(4), and the geometry of the ligands around the nickel ion, we decided to carry out an X-ray structural analysis of $[\mathrm{Ni(2\text{-}methyltetrazole)_6}]\ (\mathrm{BF_4})_2$ {during the rest of this article abbreviated as $[\mathrm{Ni(2MeTz)_6}]\ (\mathrm{BF_4})_2$}.

Experimental. Crystals grown from solution of absolute ethanol and triethyl orthoformate, containing stoichiometric amounts of 2-methyltetrazole (van den Heuvel, Franke, Everstijn & Zuur, 1983) and the salt $\mathrm{Ni(BF_4)_2.6H_2O}$ (van Leeuwen & Groeneveld, 1967); $0{\cdot}3 \times 0{\cdot}18 \times 0{\cdot}18$ mm, Enraf–Nonius CAD-4, cell dimensions from setting angles of 24 reflections with $12 < \theta < 15°$, 1651 reflections h,k,l, $l \geq 0$, $k \geq h$, measured for $2 < \theta < 25°$, graphite-monochromated Mo $K\alpha$, no absorption correction (relative transmission 0·98—1·02); relative intensities of three standard reflections varied by <0·06; 937 independent reflections, 772 significant $[I > 2\sigma(I)]$, $R_{\mathrm{int}} = 0{\cdot}02$, Patterson methods, least-squares refinement on F, difference Fourier syntheses; $\mathrm{BF_4}$ appeared to occur in two

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* Tetrazoles as Ligands. V. Part IV: Franke, Haasnoot & Zuur (1982).

† Requests for reprints should be sent to this author.

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positions related by a pseudo-mirror plane, H located in difference Fourier syntheses, full-matrix anisotropic (H isotropic) (101 parameters) until ratio of maximum LS shift to error < 0.10, maximum height in final ΔF synthesis 0·35 e$Å^{-3}$, statistical height 0·08 e$Å^{-3}$; $wR = 0.04$ ($w = 1$), $S = 1.51$, atomic scattering factors for neutral atoms (*International Tables for X-ray Crystallography,* 1974), corrected for anomalous dispersion.*

All calculations were carried out using the Leiden University Amdahl and IBM computers with the aid of a set of computer programs written or modified by Mrs E. W. Rutten-Keulemans, Dr R. A. G. de Graaff and Dr G. C. Verschoor.

Discussion. Positional parameters are given in Table 1.

The $[Ni(2MeTz)_6]^{2+}$ cation exists as a discrete unit with the six ligands arranged in an almost perfect octahedral array. The octahedron is slightly flattened with angles between 89·0 (1) and 91·0 (1)°. The atomic numbering of the molecule is indicated in Fig. 1.

As found in other complexes with substituted tetrazoles (Gilbert & Brubaker, 1963; Biefield & Gilbert, 1971; Franke & Groeneveld, 1981) coordination takes place *via* the N(4) atom with a coordination distance of 2·095 (3) Å. Some intramolecular distances (<2·2 Å) and bond angles in the molecule are listed in Table 2.

Table 1. *Atomic fractional positional parameters* ($\times 10^4$ *for* Ni, N, C, $\times 10^3$ *for* H, B, F) *and equivalent isotropic temperature factors* ($Å^2 \times 10^2$ *for* Ni, N, C, $Å^2 \times 10$ *for* H, B, F)

E.s.d.'s are in parentheses.

	x	y	z	B_{eq}†
Ni	0‡	0‡	0‡	200 (2)
N(4)	1030 (3)	1752 (3)	1670 (4)	269 (8)
N(3)	458 (3)	2509 (3)	1952 (4)	319 (9)
N(2)	1358 (3)	3578 (3)	2863 (4)	325 (9)
N(1)	2512 (3)	3585 (3)	3205 (4)	416 (11)
C(5)	2268 (4)	2430 (4)	2439 (6)	384 (13)
C(6)	1133 (5)	4709 (4)	3330 (8)	497 (17)
H(4)	288 (4)	213 (4)	239 (5)	42 (9)
H(1)	164 (5)	539 (5)	251 (7)	70 (13)
H(2)	23 (5)	440 (5)	326 (7)	68 (14)
H(3)	147 (5)	503 (5)	459 (7)	76 (14)
B	667‡	333‡	163 (1)	53 (3)
F(1)(ax)	667‡	333‡	−11 (2)	125 (6)
F(1)*(ax)	667‡	333‡	327 (2)	186 (13)
F(2)	716 (2)	262 (1)	236 (1)	150 (7)
F(2)*	720 (2)	264 (2)	89 (2)	160 (10)

The site-occupancy factors for the atoms are all 1 except those for the F atoms which are 0·57 for F and 0·43 for F*.

† $B = \frac{8}{3}\pi^2$ trace **U**.

‡ Parameters were held fixed.

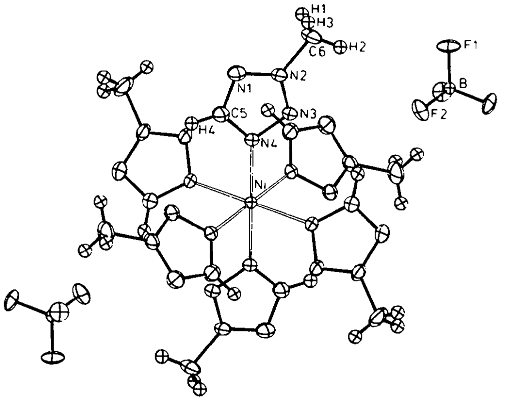

Fig. 1. Perspective view of $[Ni(2MeTz)_6](BF_4)_2$ with atoms drawn on a 50% probability scale except the hydrogen, boron and fluorine atoms which are drawn on a 25% scale (*ORTEP*: Johnson, 1965).

Table 2. *Distances* (Å) *and bond angles* (°)

E.s.d.'s are in parentheses.

Ni–N(4)	2·095 (3)	N(1)–C(5)	1·311 (4)
N(4)–N(3)	1·322 (3)	C(5)–H(4)	0·91 (4)
N(4)–C(5)	1·333 (4)	C(6)–H(1)	0·91 (5)
N(3)–N(2)	1·300 (4)	C(6)–H(2)	0·90 (5)
N(2)–C(6)	1·463 (5)	C(6)–H(3)	0·97 (5)
N(2)–N(1)	1·324 (4)		
Ni–N(4)–N(3)	118·6 (2)	N(1)–C(5)–N(4)	112·5 (3)
Ni–N(4)–C(5)	134·9 (2)	N(4)–C(5)–H(4)	123 (2)
N(3)–N(4)–C(5)	106·1 (3)	N(2)–C(6)–H(1)	106 (3)
N(4)–N(3)–N(2)	105·7 (3)	N(2)–C(6)–H(2)	108 (3)
N(3)–N(2)–N(1)	114·1 (3)	N(2)–C(6)–H(3)	109 (3)
N(3)–N(2)–C(6)	122·0 (3)	N(1)–N(2)–C(6)	123·8 (3)
C(5)–N(1)–N(2)	101·7 (3)	N(1)–C(5)–H(4)	124 (2)
B–F(1)(ax)	1·24 (1)	F(1)(ax)–F(2)	2·13 (1)
B–F(1)*(ax)	1·16 (2)	F(1)*(ax)–F(2)*	2·08 (2)
B–F(2)	1·300 (9)	F(1)*(ax)–F(2)	1·36 (1)
B–F(2)*	1·32 (1)	F(2)*–F(2)	1·05 (1)
F(1)(ax)–F(2)*	1·40 (2)		
F(1)(ax)–B–F(2)	113·4 (7)	F(1)(ax)–B–F(2)*	66·3 (8)
F(1)(ax)–B–F(1)*(ax)	180·00	F(2)–B–F(2)*	47·2 (6)

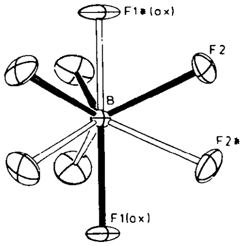

Fig. 2. Perspective view of the BF_4 and BF_4^* groups (*ORTEP*: Johnson, 1965). The BF_4^* group is indicated by open bonds. (Atoms are drawn on a 50% probability scale.)

The tetrafluoroborate anion, which was found to be disordered, is represented in Fig. 2. Distances and bond angles between the atoms in the two possible orientations indicate nearly tetrahedral geometry. From the refined multiplicities of the F and F* atoms the occupancy factors for the two orientations are found to

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38236 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Comparison of mean bond lengths* (Å) *and angles* (°) *in some tetrazole-containing compounds*

	HTz	NaTz	[Fe(1PrTz)$_6$] (BF$_4$)$_2$	[Zn(1MeTz)$_2$ Cl$_2$]	[Ni(2MeTz)$_6$] (BF$_4$)$_2$
M–N(4)	—	—	2·153	2·05	2·095
N(4)–N(3)	1·33	1·348	1·369	1·34	1·322
N(4)–C(5)	1·33	1·329	1·328	1·30	1·333
N(3)–N(2)	1·30	1·310	1·297	1·29	1·300
N(2)–N(1)	1·33	1·348	1·337	1·34	1·324
N(1)–C(5)	1·30	1·329	1·326	1·30	1·311
N(3)–N(4)–C(5)	108·5	104·3	105·7	106	106·1
M–N(4)–C(5)	—	—	130·2	133	134·9
M–N(4)–N(3)	—	—	124·1	121	118·6
N(4)–N(3)–N(2)	107·6	109·5	109·8	111	105·7
N(3)–N(2)–N(1)	107·8	109·5	107·0	106	114·1
C(5)–N(1)–N(2)	109·4	104·3	109·1	108	101·7
N(1)–C(5)–N(4)	106·7	112·5	108·4	109	112·5

be 0·57 and 0·43. The very large temperature parameters of the fluoroborate anions are not unusual in hexacoordinated compounds in which the anions are very weakly bonded to the cations.

There is a reasonable agreement between the geometries of the tetrazole rings as established in the literature {Table 3, data taken from van der Putten, Heijderijk & Schenk (1974) for HTz; Palenik (1963) for NaTz; Franke (1982) for [Fe(1-propyltetrazole)$_6$](BF$_4$)$_2$ and from Baenziger & Schultz (1971) for [Zn(1MeTz)$_2$Cl$_2$]} and the bond distances and angles as given in Table 2.

The structure of [Ni(2MeTz)$_6$](BF$_4$)$_2$ with its octahedral [NiN$_6$] chromphore and the space group with threefold symmetry is not unusual for transition-metal(II) complexes of azoles, *e.g.* for pyrazole and imidazole the same types of structures were reported (Santoro, Mighell, Zocchi & Reimann, 1969; Reimann, Santoro & Mighell, 1970; ten Hoedt, Driessen & Verschoor, 1983).

References

Baenziger, N. C. & Schultz, R. J. (1971). *Inorg. Chem.* **10**, 661–667.

Biefield, R. M. & Gilbert, G. L. (1971). *J. Inorg. Nucl. Chem.* **33**, 3947–3950.

Daugherty, N. A. & Brubaker, C. H. Jr (1961*a*). *J. Am. Chem. Soc.* **83**, 3779–3782.

Daugherty, N. A. & Brubaker, C. H. Jr (1961*b*). *J. Inorg. Nucl. Chem.* **22**, 193–197.

Franke, P. L. (1982). Thesis. State Univ. Leiden.

Franke, P. L. & Groeneveld, W. L. (1980*a*). *Inorg. Chim. Acta*, **40**, 111–114.

Franke, P. L. & Groeneveld, W. L. (1980*b*). *Trans. Met. Chem.* **5**, 240–244.

Franke, P. L. & Groeneveld, W. L. (1981). *Trans. Met. Chem.* **6**, 54–56.

Franke, P. L., Haasnoot, J. G. & Zuur, A. P. (1982). *Inorg. Chim. Acta*, **59**, 5–9.

Garber, L. L., Sims, L. B. & Brubaker, C. H. Jr (1968). *J. Am. Chem. Soc.* **90**, 2518–2523.

Gilbert, G. L. & Brubaker, C. H. Jr (1963). *Inorg. Chem.* **2**, 1216–1219.

Harris, A. D., Herber, R. H., Jonassen, H. B. & Wertheim, G. K. (1963). *J. Am. Chem. Soc.* **85**, 2927–2930.

Harris, A. D., Jonassen, H. B. & Archer, R. D. (1965). *Inorg. Chem.* **4**, 147–149.

Heuvel, E. J. van den, Franke, P. L., Everstijn, N. & Zuur, A. P. (1983). In preparation.

Hoedt, R. W. M. ten, Driessen, W. L. & Verschoor, G. C. (1983). *Acta Cryst.* C**39**, 71–72.

Holm, R. D. & Donnelly, P. L. (1966). *J. Inorg. Nucl. Chem.* **28**, 1887–1894.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Jonassen, H. B., Terry, J. O. & Harris, A. D. (1963). *J. Inorg. Nucl. Chem.* **25**, 1239–1243.

Labine, P. & Brubaker, C. H. Jr (1971). *J. Inorg. Nucl. Chem.* **33**, 3383–3397.

Leeuwen, P. W. N. M. van & Groeneveld, W. L. (1967). *Inorg Nucl. Chem. Lett.* **3**, 145–146.

Mihina, J. S. & Herbst, R. M. (1950). *J. Org. Chem.* **15**, 1082–1092.

Ostrovskii, V. A., Panina, N. S. Koldobskii, G. I., Gidaspov, B. V. & Shirobokov, I. Y. (1979). *Zh. Org. Khim.* **15**, 844–846.

Palenik, G. J. (1963). *Acta Cryst.* **16**, 596–600.

Putten, N. van der, Heijderijk, D. & Schenk, M. (1974). *Cryst. Struct. Commun.* **3**, 321–322.

Reimann, C. W., Santoro, A. & Mighell, A. D. (1970). *Acta Cryst.* B**26**, 521–526.

Santoro, A., Mighell, A. D., Zocchi, M. & Reimann, C. W. (1969). *Acta Cryst.* B**25**, 842–847.

Acta Cryst. (1983). C**39**, 339–341

Structure of Bis[5-hydroxymethyl-2-methyl-4-(phenylethyliminomethyl)-3-pyridinolato-*N*,*O*]copper(II), Cu(C$_{16}$H$_{17}$N$_2$O$_2$)$_2$

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(*Received* 23 *March* 1982; *accepted* 15 *November* 1982)

Abstract. $M_r = 602{\cdot}2$, monoclinic, $P2_1/c$, $a = 11{\cdot}3403$ (6), $b = 8{\cdot}916$ (2), $c = 14{\cdot}283$ (1) Å, $\beta = 90{\cdot}600$ (6)°, $Z = 2$, $V = 1444{\cdot}2$ (5) Å^3, $D_m = 1{\cdot}37$ (1), $D_x = 1{\cdot}38$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 7{\cdot}98$ mm^{-1}, $F(000) = 630$, $T = 293$ K, $R = 0{\cdot}036$ for 2860 independent reflections. The copper-atom environment is exactly square planar.

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0108-2701/83/030339-03$01.50