Acta Cryst. (1983). C**39**, 334–337

Structural Studies on Metal Complexes of Chiral Cyclen. IV. Chloro[2*R*,5*R*,8*S*,11*S*)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane]copper(II) Dichlorocuprate(I), $[Cu(C_{44}H_{60}N_4)Cl][CuCl_2]$

By Tosio Sakurai, Kimiko Kobayashi, Hidehiro Masuda, Sei Tsuboyama and Kaoru Tsuboyama

The Institute of Physical and Chemical Research (Rikagaku Kenkyusho), Wako-shi, Saitama 351, *Japan*

(*Received* 30 *June* 1982; *accepted* 2 *November* 1982)

Abstract. $M_r = 878{\cdot}41$, monoclinic, $P2_1/c$, $a = 11{\cdot}061\,(7)$, $b = 24{\cdot}410\,(19)$, $c = 17{\cdot}374\,(16)$ Å, $\beta = 108{\cdot}68\,(6)°$, $U = 4444\,(6)$ Å^3, $Z = 4$, $D_m = 1{\cdot}30$, $D_x = 1{\cdot}313\,(2)$ Mg m^{-3} at 296 K, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}175$ mm^{-1}. Final $R = 7{\cdot}8\%$ for 2279 independent reflections. The structure contains an isolated linear Cu^ICl_2 group as the counteranion. The 12-membered ring takes the [2343] form. The coordination about the Cu^{II} atom is approximately square pyramidal, but is displaced about 15% towards the trigonal-bipyramidal form.

Introduction. This paper is part of the series of investigations of metal complexes of chiral cyclens.* The chiral cyclens can be divided into four geometrical isomers, *viz.* C_4, C_1, C_i and S_4. Electronic absorption, circular dichroism and electron spin resonance spectra (ESR) of these cyclen complexes reveal that the form of the metal coordination changes gradually with chirality (Tsuboyama, Tsuboyama, Sakurai, Kobayashi, Kajikawa & Ishizu, 1982). X-ray analyses revealed that the copper(II) complex of the C_4 isomer appears as the typical square-pyramidal coordination, while that of the S_4 isomer forms an approximate trigonal bipyramid (Sakurai, Kobayashi, Hasegawa, Tsuboyama & Tsuboyama, 1982; Kobayashi, Sakurai, Hasegawa, Tsuboyama & Tsuboyama, 1982). This paper reports the structure of the copper complex with the C_i isomer.

Experimental. The Cu complex was prepared by heating a mixture of $CuCl_2.2H_2O$ (1 mmol) in absolute EtOH and tbte-(*RRSS*)-cyclen (1 mmol). Although the reaction conditions were the same as for other isomers, the resultant product was quite different. The product consists of a mixture of green and brown solids. The brown one, which was insoluble in EtOH, was removed by filtration. The green one was purified by column chromatography on Sephadex LH-60 with EtOH. The precipitate in a fraction of green effluent was recrystallized from EtOH and the single crystals (complex *A*) suitable for X-ray analysis were obtained.

When the residual effluents were collected and treated with excess $CuCl_2$ in EtOH, two additional products were obtained. One was a triclinic green crystal (complex *B*) and another was a blue-green product (complex *C*). Complex *C* was found to be $[Cu^{II}Cl\{$tbte-(*RRSS*)-cyclen$\}]^+Cl^-$, whose chemical formula differs from that of complex *A*. X-ray analysis was carried out for complex *A*.

The chemical analysis of complex *A* is consistent with the formula described in the *Abstract.* Analysis (%): obs. C 60·49, H 6·99, Cl 11·89, Cu 14·64, N 6·30; calc for $C_{44}H_{60}Cl_3Cu_2N_4$ C 60·12, H 6·88, Cl 12·16, Cu 14·46, N 6·37.

Fragile crystal sealed in glass capillary with solvent, dimensions 0·5 × 0·2 × 0·08 mm; intensity data collected on a Rigaku automated four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, three standard reflections 400, 0,14,0 and 004 measured every 150 reflections; within range $2\theta < 45°$ 2472 reflections with $|F_o| > 3\sigma(F_o)$ obtained, intensities corrected for Lorentz and polarization but not absorption, 2279 unique, 3888 unobserved; structure solved by heavy-atom method, refined by block-diagonal least squares based on $|F_o|$, unit weight given to all reflections, counteranion found to have $CuCl_2$ form by difference Fourier synthesis, anisotropic temperature factors used for all non-H atoms, H-atom coordinates generated assuming standard bond lengths and angles, included in the structure-factor calculation with isotropic temperature factors but coordinates not refined; $F(000) = 1844$, atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974), final *R* and *wR* 7·8 and 8·2% respectively; crystallographic calculations performed on a FACOM 230-75 computer of this Institute using *UNICS* III program system (Sakurai & Kobayashi, 1979).

---

* Abbreviations: cyclen: 1,4,7,10-tetraazacyclododecane; tbte-cyclen: 1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane; C_4 isomer: tbte-(*RRRR*)- or tbte-(*SSSS*)-cyclen; C_1 isomer: tbte-(*RRRS*)- or tbte-(*SSSR*)-cyclen; C_i isomer: tbte-(*RRSS*)-cyclen; S_4 isomer: tbte-(*RSRS*)-cyclen.

0108-2701/83/030334-04$01.50

Discussion. The atomic parameters are shown in Table 1.*

Fig. 1 is a stereoscopic drawing of the molecule (Johnson, 1965). The 12-membered ring of the free molecule of tbte-(*RRSS*)-cyclen has a distorted square [3333]† conformation (Hiramatsu, Sakurai, Tsuboyama & Tsuboyama, 1979). However, it is not suitable for the formation of the complex because the ring forms an armchair conformation, and the N atoms at the *S* side of the ring are situated at the opposite side of the ring-plane from those at the *R* side of the ring. Upon the formation of the metal complex, two of the bonds to the N atoms on one side of the ring are rotated so that all N atoms are on the same side. The resultant ring conformation is [2343]. The coordination to the Cu atom is shown in Fig. 2. The four N atoms are not coplanar, the dihedral angle between the N(1),N(4),N(7) and N(1),N(7),N(10) planes being 6·0 (7)°. Angles N(1)–Cu(1)–N(7) and N(4)–Cu(1)–N(10) are 147·9 (2) and 153·6 (5)° respectively. Therefore, the conformation is an approximate square pyramid (s.p.), but is displaced about 15% along the Berry coordinate from the s.p. towards the trigonal bipyramid (t.b.) (Holmes & Deiters, 1977). The Cu(1)–Cl(1) distance, 2·381 (5) Å, and the mean Cu–N distance, 2·08 Å, are near the s.p. values. The Cu atom is 0·528 (7) Å above the mean plane formed by the four N atoms. These results are consistent with the optical and ESR observations.

Table 1. *Atomic parameters*

Positional parameters are multiplied by 10^4. The equivalent isotropic temperature factor is defined by $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j)$.

	x	y	z	B_{eq}(Å^2)
Cu(1)	0 (2)	−556 (1)	−3293 (1)	4·7 (0·1)
Cl(1)	−1518 (4)	−181 (2)	−4476 (3)	5·5 (0·2)
Cl(2)	3168 (5)	−1189 (3)	−904 (3)	8·3 (0·2)
N(1)	−749 (11)	−1321 (5)	−3116 (7)	4·8 (0·5)
N(4)	1229 (10)	−1003 (5)	−3726 (7)	4·4 (0·5)
N(7)	1467 (12)	14 (5)	−2897 (7)	4·8 (0·5)
N(10)	−678 (11)	−269 (6)	−2379 (7)	4·9 (0·5)
C(2)	175 (16)	−1777 (7)	−3205 (11)	5·9 (0·7)
C(3)	1483 (16)	−1491 (7)	−3146 (10)	5·4 (0·6)
C(5)	2430 (13)	−654 (7)	−3610 (10)	5·0 (0·6)
C(6)	2673 (14)	−299 (7)	−2834 (10)	5·4 (0·6)
C(8)	1517 (15)	135 (7)	−2017 (10)	5·4 (0·6)
C(9)	136 (14)	238 (7)	−2036 (11)	5·7 (0·6)
C(11)	−305 (15)	−775 (7)	−1821 (10)	5·9 (0·7)
C(12)	−973 (18)	−1288 (8)	−2281 (10)	6·6 (0·7)
C(1)1	−2052 (16)	−1371 (7)	−3799 (11)	6·1 (0·7)
C(1)2	−2672 (16)	−1936 (8)	−3856 (11)	6·5 (0·7)
C(1)3	−3517 (17)	−2030 (9)	−3387 (13)	7·7 (0·8)
C(1)4	−4182 (22)	−2538 (11)	−3521 (14)	10·6 (1·1)
C(1)5	−4029 (22)	−2928 (10)	−4033 (15)	10·7 (1·1)
C(1)6	−3152 (21)	−2841 (10)	−4459 (14)	10·1 (1·0)
C(1)7	−2471 (20)	−2321 (9)	−4393 (12)	8·4 (0·9)
C(2)1	393 (19)	−2231 (8)	−2566 (12)	7·9 (0·8)
C(2)2	980 (25)	−2722 (9)	−2881 (16)	10·9 (1·2)
C(4)1	615 (14)	−1130 (7)	−4649 (9)	5·4 (0·6)
C(4)2	1401 (15)	−1551 (7)	−4975 (9)	5·0 (0·6)
C(4)3	1389 (19)	−2108 (7)	−4864 (12)	6·7 (0·8)
C(4)4	2089 (19)	−2459 (8)	−5216 (12)	7·9 (0·9)
C(4)5	2860 (20)	−2225 (10)	−5607 (13)	8·7 (0·9)
C(4)6	2877 (19)	−1657 (9)	−5738 (12)	8·1 (0·8)
C(4)7	2104 (16)	−1292 (8)	−5414 (10)	5·8 (0·7)
C(5)1	3662 (15)	−1005 (8)	−3504 (11)	6·3 (0·7)
C(5)2	4582 (16)	−616 (9)	−3817 (13)	7·8 (0·8)
C(7)1	1132 (16)	481 (7)	−3514 (9)	5·5 (0·6)
C(7)2	2085 (17)	934 (7)	−3453 (11)	6·2 (0·7)
C(7)3	3130 (16)	869 (10)	−3697 (12)	8·3 (0·9)
C(7)4	3850 (20)	1372 (12)	−3699 (12)	10·4 (1·0)
C(7)5	3425 (27)	1880 (10)	−3508 (14)	12·4 (1·2)
C(7)6	2337 (26)	1928 (12)	−3309 (16)	13·0 (1·3)
C(7)7	1673 (19)	1440 (9)	−3257 (11)	8·0 (0·8)
C(8)1	2394 (16)	632 (8)	−1604 (11)	6·8 (0·7)
C(8)2	2758 (21)	551 (10)	−644 (11)	9·1 (0·9)
C(10)1	−2096 (15)	−131 (8)	−2699 (11)	6·8 (0·7)
C(10)2	−2605 (16)	249 (8)	−2166 (11)	6·6 (0·7)
C(10)3	−2522 (20)	808 (8)	−2203 (16)	9·5 (1·0)
C(10)4	−3104 (24)	1125 (13)	−1717 (21)	16·7 (1·6)
C(10)5	−3672 (28)	889 (17)	−1235 (15)	19·1 (1·8)
C(10)6	−3855 (23)	312 (17)	−1290 (15)	16·6 (1·7)
C(10)7	−3279 (20)	−41 (11)	−1774 (15)	10·6 (1·1)
C(11)1	−569 (18)	−711 (9)	−982 (11)	7·6 (0·8)
C(11)2	104 (21)	−1148 (11)	−393 (11)	10·1 (1·0)
Cu(2)	4791 (2)	−1375 (1)	−1196 (1)	6·5 (0·1)
Cl(3)	6425 (6)	−1551 (3)	−1503 (4)	10·4 (0·3)

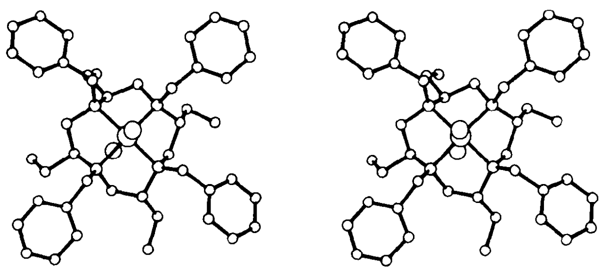


Fig. 1. A stereoscopic drawing of the molecule.

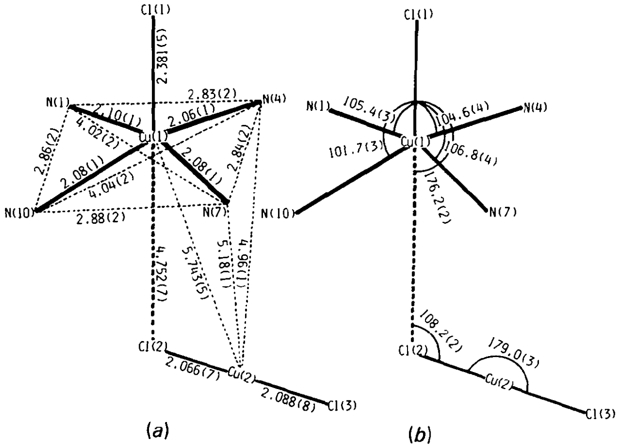


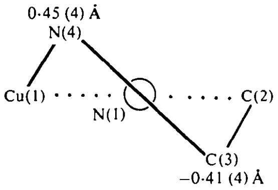
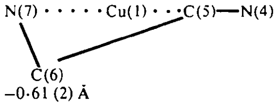
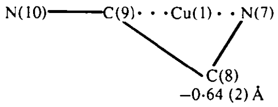
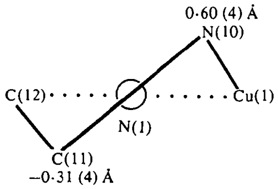
Fig. 2. The bond parameters about the Cu atoms. (*a*) Bond lengths (Å). (*b*) Bond angles (°).

---

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38215 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The conformation type is expressed by a series of numbers within square brackets, each giving the number of bonds in one side (Dale, 1973).

Table 2. *Conformations of the five-membered rings*

Ring	Conformation*	Pseudorotation angle P [in units of $(2\pi/20)$radian],* present complex
	${}^{4}_{3}T(\delta)$	12
	${}_{3}E(\varepsilon)$	11
	${}_{2}E(\varepsilon)$	19
	${}^{1}_{2}T(\lambda)$	18

* These notations are those given by Altona & Sundaralingam (1972).

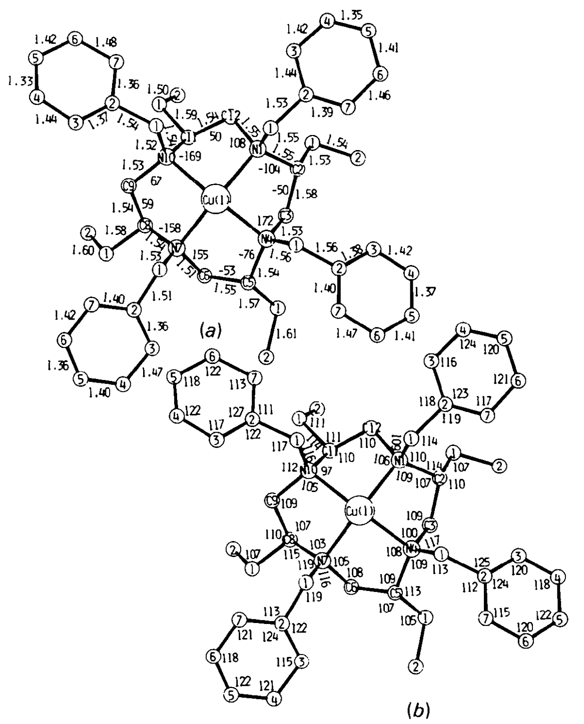


Fig. 3. The bond parameters in tbte-cyclen. (*a*) Bond lengths (Å) and torsion angles (°). Torsion angles around the ring are given by the figures inside the ring. Other values are bond lengths. (*b*) Bond angles (°). The standard deviations are: bond lengths (Å): N—C 0·02, C—C(ring) 0·03, C—C(ring-ethyl) 0·03, C—C(ethyl) 0·03, N—C(benzyl) 0·02, C—C(benzyl) 0·03, C—C(benzyl group) 0·03. Torsion angles 2°. Bond angles (°): in the ring 1, in the ring-ethyl 1, in the ethyl 2, in the ring-benzyl 1, in the benzyl group 2.

Each five-membered chelate ring has a different form as shown in Table 2. The bond parameters of the tbte-cyclen part are shown in Fig. 3.

The conformations of the benzyl groups are similar to those observed in the Cu^{II} complex of the C_4 isomer. The conformational energy of the tbte-cyclen part was calculated with a molecular mechanical method. In spite of the irregular shape of the molecule, the calculated energy is not much different from those of the other isomers.

The disposition of the anion part is visualized in Fig. 2. The anion group has an almost linear shape [179·0 (3)°]. The line connecting the Cl(1), Cu(1) and Cl(2) atoms is nearly straight, deviating only by 3·8 (2)° from linearity. The Cu(1)—Cl(2) distance, 4·752 (7) Å, is similar to the length found in the Cu^{II} complex of the S_4 isomer. The Cu(1)—Cu(2) separation is 5·743 (5) Å.

The Cu(2) atom in the anion moiety is univalent and takes part in linear two-coordination. Further support for the oxidation number of these two copper ions was provided by inspection of magnetic properties. That is, the magnetic moment, $\mu_{\rm eff} = 1{\cdot}86$ BM (1BM ≡ $9{\cdot}27 \times 10^{-24}$ JT^{-1}), shows that one of the copper ions is diamagnetic and the ESR spectrum of the complex was found to be identical with that of the above-mentioned complex *C*, which contains only one Cu^{II} ion. The mean Cu(2)—Cl distance in the anion group, 2·077 Å, is comparable to those found in the Cu^{II} or Cu^{I} complexes containing linear Cu^{I}Cl$_2$ as the counteranion(s) (*ca* 2 Å) (Marsh & Trotter, 1971; Kaiser, Brauer & Schroder, 1974; Francisco, Santos, Lechat & Masabini, 1981). The shortest one so far reported is 1·96 (1)Å in the complex of tris(imidotetraphenyldithiodiphosphino-*S*,*S*′)tetracopper(I) dichlorocuprate(I) (Huber, Post & Siiman, 1978).

The facile reduction of Cu^{II} and the scheme for the formation of the mixed-valence complex will be discussed in a separate paper.

References

Altona, C. & Sundaralingam, M. (1972). *J. Am. Chem. Soc.* **94**, 8205–8212.

Dale, J. (1973). *Acta Chem. Scand.* **27**, 1115–1129.

Francisco, R. H. P., Santos, R. H. de A., Lechat, J. R. & Masabini, A. C. (1981). *Acta Cryst.* B**37**, 232–234.

Hiramatsu, H., Sakurai, T., Tsuboyama, K. & Tsuboyama, S. (1979). *Acta Cryst.* B**35**, 1241–1244.

Holmes, R. R. & Deiters, J. A. (1977). *J. Am. Chem. Soc.* **99**, 3318–3326.

Huber, C. P., Post, M. L. & Siiman, O. (1978). *Acta Cryst.* B**34**, 2629–2632.

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.* **B38**, 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.* **B38**, 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), $[Ni(C_2H_4N_4)_6](BF_4)_2$*

BY E. J. VAN DEN HEUVEL, P. L. FRANKE, G. C. VERSCHOOR AND A. P. ZUUR†

Department of Chemistry, Gorlaeus Laboratories, State University of Leiden, PO Box 9502, 2300 *RA Leiden, The Netherlands*

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

Abstract. $C_{12}H_{24}N_{24}Ni.2BF_4$, $M_r = 736{\cdot}80$, $P\bar{3}$, $a = b = 11{\cdot}311$ (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 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 $[Ni(2\text{-methyltetrazole})_6]$ $(BF_4)_2$ {during the rest of this article abbreviated as $[Ni(2MeTz)_6]$ $(BF_4)_2$ }.

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 $Ni(BF_4)_2.6H_2O$ (van Leeuwen & Groeneveld, 1967); 0·3 × 0·18 × 0·18 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 $[I > 2\sigma(I)]$, $R_{\text{int}} = 0{\cdot}02$, Patterson methods, least-squares refinement on F, difference Fourier syntheses; BF_4 appeared to occur in two

---

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

† Requests for reprints should be sent to this author.

0108-2701/83/030337-03$01.50