Hexakis(imidazole)nickel(II) Bis(tetrafluoroborate)

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Abstract. $Ni(C_3N_2H_4)_6(BF_4)_2$, monoclinic, $P2_1/n$, $a = 11\cdot303$ (9), $b = 7\cdot234$ (4), $c = 16\cdot223$ (7) Å, $\beta = 90\cdot42$ (4)°, $Z = 2$, M.W. 640·83, $d_o = 1\cdot614$, $d_c = 1\cdot603$ g cm^{-3}, $\mu(Mo\ K\alpha) = 8\cdot3$ cm^{-1}, $V = 1326\cdot5$ Å^3. Least-squares refinement resulted in a final R_w value of 0·035 for 1574 observed independent reflexions. The Ni ions are octahedrally surrounded by six imidazole ligands.

Introduction. The complex was obtained by blending alcoholic solutions of imidazole and the hexahydrated $Ni(BF_4)_2$ salt (Reedijk, 1969). Triethyl orthoformate was added as dehydrating agent (van Leeuwen & Groeneveld, 1967). Crystals were grown by slowly decreasing the temperature of the alcoholic solution.

Preliminary Weissenberg investigations showed the Laue group to be $2/m$. 2461 reflexion intensities were recorded up to $\theta = 25°$ with an Enraf–Nonius three-circle single-crystal diffractometer, using graphite-monochromatized Mo $K\alpha$ radiation. Systematic absences were $h0l$, $h+l$ odd, and $0k0$, k odd, indicating space group $P2_1/n$. The measurements were carried out at room temperature on a banana-shaped crystal

approximately $0\cdot2 \times 0\cdot05 \times 0\cdot05$ mm. A correction was made for absorption effects according to de Graaff (1973). Transmission coefficients varied from 0·89 to 0·97. The reflexion intensities were reduced to F_o values, taking into account Lorentz and polarization effects. 1574 reflexions with $I > 2\sigma(I)$ were considered as observed.

Scattering factors for Ni were taken from Cromer & Waber (1965) and for the light atoms from *International Tables for X-ray Crystallography* (1962). The real part of the anomalous dispersion of Mo $K\alpha$ radiation was taken into account. Owing to the special position of Ni the structure was easily solved from a Patterson synthesis. C and N atoms were distinguished in a Fourier map. Least-squares refinement was performed with the observed reflexions. The function minimized during the refinement was $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma(F_o)]^{-2}$. Discrepancy indices are defined as $R = \sum ||F_o| - |F_c||/\sum |F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$. After isotropic refinement of the non-hydrogen atoms, H atoms were placed at calculated positions at a distance of 0·95 Å from the imidazole atoms.

Table 1. *Fractional coordinates* ($\times 10^4$) *of non-hydrogen atoms with anisotropic temperature factor components* ($\times 10^3$)

The anisotropic temperature factor has the form:

$$\exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^*)\}.$$

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
Ni	0*	0*	0*	27 (0)	36 (0)	34 (0)	0*	0*	−3 (1)
N(A1)	1132 (3)	1673 (4)	745 (2)	30 (2)	41 (2)	40 (2)	−5 (4)	−3 (4)	−2 (3)
C(A2)	1266 (4)	1654 (7)	1588 (2)	46 (3)	47 (3)	42 (3)	−6 (5)	−12 (5)	−15 (4)
C(A3)	2183 (4)	2757 (8)	1814 (3)	62 (3)	61 (4)	58 (3)	5 (6)	−20 (6)	−36 (5)
N(A4)	2620 (4)	3466 (6)	1100 (3)	39 (2)	53 (3)	91 (3)	−26 (4)	−30 (5)	−19 (5)
C(A5)	1960 (4)	2787 (7)	475 (3)	42 (3)	52 (3)	56 (3)	−22 (5)	−2 (5)	0 (5)
N(B1)	288 (3)	1724 (6)	−1042 (2)	38 (2)	39 (2)	37 (2)	−3 (4)	1 (4)	0 (3)
C(B2)	1234 (4)	1734 (7)	−1561 (3)	59 (3)	59 (4)	57 (3)	2 (6)	7 (6)	47 (5)
C(B3)	1065 (5)	2893 (8)	−2176 (3)	81 (4)	58 (4)	48 (3)	−12 (6)	0 (5)	59 (6)
N(B4)	−23 (4)	3687 (6)	−2056 (2)	96 (3)	55 (3)	47 (3)	−25 (5)	29 (4)	−36 (5)
C(B5)	−446 (4)	2941 (7)	−1360 (3)	51 (3)	47 (3)	45 (3)	−8 (5)	21 (5)	−5 (5)
N(C1)	−1501 (3)	1597 (6)	331 (2)	34 (2)	39 (2)	40 (2)	1 (4)	−4 (4)	7 (3)
C(C2)	−1546 (4)	2961 (7)	915 (3)	46 (3)	46 (3)	54 (3)	3 (5)	−13 (5)	6 (5)
C(C3)	−2640 (4)	3642 (7)	995 (3)	45 (3)	51 (3)	52 (3)	22 (5)	−14 (5)	13 (5)
N(C4)	−3304 (4)	2691 (7)	440 (2)	35 (2)	83 (3)	79 (3)	38 (5)	21 (5)	15 (4)
C(C5)	−2602 (4)	1481 (7)	48 (3)	35 (3)	62 (3)	62 (3)	18 (5)	−27 (6)	−15 (5)
F(1)	5603 (4)	1194 (6)	8511 (2)	142 (5)	175 (4)	106 (3)	181 (6)	−99 (5)	−52 (5)
F(2)	5464 (4)	4142 (6)	8610 (2)	151 (3)	162 (4)	121 (3)	−224 (6)	12 (5)	−45 (5)
F(3)	4431 (3)	2484 (6)	9440 (2)	79 (2)	177 (4)	72 (2)	9 (5)	26 (5)	40 (3)
F(4)	3973 (3)	2589 (6)	8096 (2)	58 (2)	136 (3)	97 (2)	−10 (4)	−32 (5)	−47 (3)
B	4836 (5)	2559 (11)	8669 (4)	39 (3)	80 (5)	63 (4)	7 (7)	−42 (8)	9 (6)

* Parameter was held fixed.

Full-matrix anisotropic refinement of the heavy atoms resulted in $R_w = 0.035$ and $R = 0.048$. The R_w value including non-observed (235) and non-significant (487) reflexions is 0.038. No extinction corrections were made.

Final parameters of the non-hydrogen atoms are listed in Table 1. The coordinates of the H atoms are in Table 2. For the H atoms a B value of 4.0 Å^2 was assumed. The scale factor was 0.717. Final shifts of the parameters were less than 1% of the estimated standard deviation. A difference Fourier map showed

no peaks higher than three times the statistical height of 0.1 e Å^{-3}.[*]

Table 2. *Fractional coordinates of the hydrogen atoms*
$(\times 10^4)$

	x	y	z
H(A2)	787	969	1958
H(A3)	2464	2988	2358
H(A4)	3271	4288	1052
H(A5)	2078	3079	−89
H(B2)	1924	1000	−1488
H(B3)	1592	3134	−2616
H(B4)	−400	4583	−2396
H(B5)	−1188	3255	−1127
H(C2)	−881	3374	1225
H(C3)	−2896	4585	1361
H(C4)	−4127	2852	344
H(C5)	−2859	659	−373
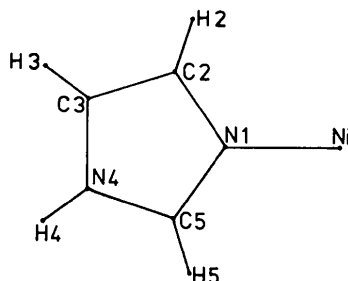
Fig. 1. Atomic numbering of the imidazole ligands.

Table 3. *Interatomic distances (Å), angles (°) and least-squares planes*

(a) Coordination of nickel

Ni–N(A1)	2.131	N(A1)–Ni–N(B1)	91.33
Ni–N(B1)	2.127	N(B1)–Ni–N(C1)	90.53
Ni–N(C1)	2.125	N(C1)–Ni–N(A1)	91.45

(b) Tetrafluoroborate anion

B–F(1)	1.340	F(1)–B–F(2)	105.7
B–F(2)	1.351	F(1)–B–F(3)	112.0
B–F(3)	1.336	F(1)–B–F(4)	110.3
B–F(4)	1.342	F(2)–B–F(3)	106.5
		F(2)–B–F(4)	108.6
		F(3)–B–F(4)	113.4

(c) Imidazole ligands

	A	B	C
N(1)–C(2)	1.375	1.366	1.369
C(2)–C(3)	1.357	1.316	1.339
C(3)–N(4)	1.362	1.372	1.355
N(4)–C(5)	1.347	1.342	1.344
C(5)–N(1)	1.313	1.313	1.326

	A	B	C
Ni—N(1)–C(2)	128.3	128.2	126.9
Ni—N(1)–C(5)	125.9	127.3	128.9
C(5)–N(1)–C(2)	105.3	104.4	104.2
N(1)–C(2)–C(3)	109.9	111.2	111.9
C(2)–C(3)–N(4)	105.8	106.5	104.8
C(3)–N(4)–C(5)	107.5	106.0	108.6
N(4)–C(5)–N(1)	111.4	111.9	110.5

(d) Least-squares planes of the ligands

Imidazole A
$$0.6260x - 0.7762y - 0.0750z + 0.2367 = 0$$
Imidazole B
$$-0.4255x - 0.7274y - 0.5383z + 0.1467 = 0$$
Imidazole C
$$-0.2049x - 0.6881y + 0.6960z + 0.0768 = 0$$

Fig. 2. Stereoscopic projection of one molecular unit.

Discussion. There are three independent imidazole ligands: *A*, *B* and *C*. The atomic numbering of the ligand is indicated in Fig. 1. Fig. 2 is a stereoscopic projection of one molecular unit. Geometric entities are given in Table 3. The Ni ion is octahedrally surrounded by six imidazole ligands. Contrary to the results of earlier investigations on metal(II) hexakis-(imidazole) cations (Santoro, Mighell, Zocchi & Reimann, 1969; Mighell & Santoro, 1971; Strandberg & Lundberg, 1971) no threefold axis is present. The geometry of the cation, however, shows only very slight deviations from the ideal $\bar{3}$ symmetry. No significant differences in bond distances and angles with respect to reported values and to those of imidazole (Martínez-Carrera, 1966) are found. The cations are surrounded by 12 anions, the shortest anion–cation contacts being F(1)–N(*B*4 at $\bar{x}+\frac{1}{2}, y-\frac{1}{2}, \bar{z}+\frac{1}{2}$) 3·04 Å, F(2)–N(*A*4 at $\bar{x}+1, \bar{y}+1, \bar{z}+1$) 2·81 Å and F(3)–N(*C*4 at $x+1, y, z+1$) 3·03 Å. Each anion is surrounded by six cations. The shortest cation–cation contact is C(*B*3)–C(*C*3 at $x+\frac{1}{2}, \bar{y}+\frac{1}{2}, z-1$) 3·50 Å. The very large temperature parameters of the fluoroborate anion are not unusual in hexasolvated coordination compounds in which the anions are very weakly bonded to the cations.

This investigation has been undertaken to support the study of e.p.r. spectra of hexasolvated metals of the first transition series. Reedijk & Nieuwenhuyse (1972) described powder-e.p.r. spectra of these compounds and the single-crystal spectra are the subject of investigation at our laboratory (Vermaas, 1975).

All calculations were performed on the IBM 370/158 computer of the University of Leiden with programs developed in our laboratory, partially based on *ORFLS* (Busing & Levy, 1962) and *ORTEP* (Johnson, 1965).

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β-Tetraphosphorus Pentasulphide

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Abstract. P_4S_5, monoclinic, $P2_1/m$, $a=6\cdot389$ (3), $b=10\cdot966$ (5), $c=6\cdot613$ (3) Å, $\beta=115\cdot65$ (6)°, $U=417\cdot66$ Å³, $Z=2$, $D_x=2\cdot26$ g cm⁻³. The structure of a new isomer has been determined by direct methods and refined to an R of 0·029 for 581 unique diffractometer data. The molecular geometry is analogous to that in As_4S_5, but quite unlike that in α-P_4S_5 and P_4Se_5. The cage structure possesses approximate *mm* symmetry, and consists of two PPSPS rings fused with two (PS)₃ rings. Mean bond lengths (corrected for libration) and angles for *mm* symmetry are: P–S, 2·117 (4), 2·116 (3), 2·130 (4); P–P, 2·295 (5) Å; P–S–P, 115·5 (2), 105·4 (1); S–P–S, 97·6 (2), 107·4 (1), 104·6 (1); S–P–P, 102·2 (2)°.

Introduction. Fourier transform ³¹P n.m.r. studies (Griffin & Sheldrick, 1976) have recently established the existence of several new molecular phosphorus sulphides. Two isomers of formula P_4S_5 were found; α-P_4S_5 gives an ABCX spectrum consistent with the reported structure (Vos, Olthof, van Bolhuis & Botterweg, 1965), and the new isomer β-P_4S_5 gives an A_2X_2 spectrum consistent with the structure reported here.

Crystals were obtained as elongated golden yellow platelets by cooling of a solution in CS_2. Intensities were determined with an automated Syntex $P2_1$ four-circle diffractometer, Cu $K\alpha$ radiation and graphite