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The Crystal and Molecular Structure of Anilinebis(difluoroborondimethylglyoximato)nickel(II)

By Robert S. Vagg and Edward C. Watton

School of Chemistry, Macquarie University, North Ryde, NSW 2113, *Australia*

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$C_{14}H_{19}B_2F_4N_5NiO_4$ is monoclinic, space group $P2_1/c$, with $a = 20{\cdot}21$ (4), $b = 9{\cdot}94$ (2), $c = 19{\cdot}41$ (4) Å, $\beta = 95{\cdot}9$ (2)°, $Z = 8$. The structure was refined to $R = 0{\cdot}073$ for 3443 photographic reflexions. The complex is dimeric [Ni—Ni 3·654 (2) Å] with the two formula units non-equivalent. The Ni atoms are each surrounded by four N atoms of the closely planar macrocycle [average, Ni—N 1·871 (7) Å, N—Ni—N 81·9 (3) and 97·6 (3)°] and one aniline N [Ni—N 2·724 (9) and 2·602 (10) Å] to form an irregular square pyramid. The Ni atoms are displaced 0·118 and 0·138 Å out of the N equatorial planes towards the aniline N atoms, the coordination of the latter being sterically hindered by BF_2 groups. The N_4 planes of the two macrocycles are parallel and are rotated 98·5° and translated 0·56 Å relative to each other. There are several C···O intermolecular contacts in the dimer below 3·25 Å.

Introduction

Bis(difluoroborondimethylglyoximato)nickel(II), Ni(dmgBF$_2$)$_2$, has been shown to be dimeric both in solution (Charlson, Stephens, Vagg & Watton, 1977) and in the solid state (Stephens & Vagg, 1977*a*). Graddon & Siddiqi (1976) provided evidence for the formation only of 1:1 adducts of this and like species with monodentate bases in solution, although several 2:1 complexes have been isolated in solid form (Schrauzer, 1962; Stephens, Vagg & Watton, 1978). Reaction with aniline or substituted anilines yields brightly coloured diamagnetic 1:1 adducts. An analysis of the crystal structure of the aniline adduct of Ni(dmgBF$_2$)$_2$ is described below. A preliminary report has appeared (Charlson, Stephens, Vagg & Watton, 1977).

Experimental

The complex forms as deep-scarlet needles from the reaction of Ni(dmgBF$_2$)$_2$ with aniline in warm dichloromethane.

Crystal data

$C_{14}H_{19}B_2F_4N_5NiO_4$, $M_r = 477{\cdot}7$, monoclinic, $a = 20{\cdot}21$ (4), $b = 9{\cdot}94$ (2), $c = 19{\cdot}41$ (4) Å, $\beta = 95{\cdot}9$ (2)°, $U = 3878{\cdot}6$ Å^3, $D_m = 1{\cdot}62$ (by flotation), $Z = 8$, $D_c = 1{\cdot}634$ g cm^{-3}, $F(000) = 1952$, $\mu(\mathrm{Cu}\ K\alpha) = 20{\cdot}6$ cm^{-1}. Systematic absences: $h0l$ when $l \neq 2n$, $0k0$ when $k \neq 2n$, space group $P2_1/c$.

Cell parameters were determined from oscillation photographs with Cu $K\alpha$ radiation. 4793 non-zero reflexions were recorded from layers 0–4*kl*, *h*0–5*l* and *hk*0–3 with the equi-inclination Weissenberg technique and packs of four films. Their intensities were read visually and corrected for Lorentz and polarization effects but not for absorption or extinction. Internal correlation yielded a final data set of 3443 unique reflexions.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations were carried out on a Univac 1106 computer with programs written by F. S. Stephens.

Structure determination

The structure was solved by the heavy-atom method. Isotropic refinement was by full-matrix least-squares calculations in which the function minimized was $\sum w\Delta^2$. Weights $w = (1{\cdot}00 + 0{\cdot}02|F_o| + 0{\cdot}00016|F_o|^2)^{-1}$ were used throughout. Reflexions for which $|F_o| < 0{\cdot}333|F_c|$ were omitted from the refinement.

Positions for all H atoms on the phenyl rings were calculated with C—H = 1·0 Å and those on the N and methyl C atoms were located from a difference synthesis. H atoms were placed in these positions with $B = 4{\cdot}0$ Å^2.

Due to the large number of variable parameters (656) block matrices were used during anisotropic refinement. Initially the twelve matrices contained (1) the overall scale and thermal factors and the parameters for (2) the two Ni and ten N atoms, (3)–(6) the four O_2BF_2 groups, (7), (8) the two phenyl rings, (9)–(12) the four C_4 chains. In the latter stages of

Table 1. *Final atomic coordinates (fractional:* $\times 10^4$ *for non-hydrogen atoms,* $\times 10^3$ *for* H *atoms) with e.s.d.'s in parentheses*

	x	*y*	*z*
Ni(1)	1599·6 (7)	710·7 (14)	2751·9 (6)
Ni(2)	3381·9 (7)	563·1 (13)	2582·0 (6)
N(11)	1526 (4)	2574 (7)	2635 (3)
N(12)	1485 (3)	765 (7)	1787 (3)
N(13)	1777 (3)	−1138 (7)	2858 (3)
N(14)	1838 (3)	704 (6)	3705 (3)
N(15)	358 (5)	39 (10)	3062 (5)
N(21)	3153 (3)	595 (6)	1618 (3)
N(22)	3370 (4)	−1298 (7)	2429 (3)
N(23)	3497 (3)	508 (6)	3551 (3)
N(24)	3237 (4)	2386 (6)	2742 (3)
N(25)	4645 (5)	1128 (9)	2684 (4)
B(11)	1485 (6)	3020 (11)	3869 (5)
B(12)	1309 (6)	−1656 (11)	1664 (5)
B(21)	3271 (6)	3032 (11)	1539 (5)
B(22)	3879 (7)	−1841 (10)	3576 (6)
F(111)	1650 (3)	4046 (5)	4310 (2)
F(112)	820 (3)	2623 (6)	3842 (3)
F(121)	1439 (3)	−2610 (5)	1188 (2)
F(122)	658 (3)	−1575 (6)	1787 (3)
F(211)	2995 (3)	4008 (5)	1107 (2)
F(212)	3960 (3)	2994 (6)	1584 (3)
F(221)	3852 (3)	−2900 (6)	4032 (3)
F(222)	4509 (2)	−1595 (6)	3396 (3)
O(11)	1626 (3)	3492 (6)	3169 (3)
O(12)	1528 (3)	−365 (6)	1371 (3)
O(13)	1738 (3)	−2045 (6)	2314 (3)
O(14)	1906 (3)	1841 (6)	4115 (3)
O(21)	3002 (3)	1732 (6)	1244 (3)
O(22)	3430 (3)	−2247 (6)	2449 (3)
O(23)	3619 (3)	−653 (6)	3934 (3)
O(24)	3059 (3)	3326 (5)	2238 (3)
C(11)	1470 (4)	3054 (8)	2013 (4)
C(12)	1439 (4)	1952 (9)	1501 (4)
C(13)	1935 (4)	−1587 (8)	3469 (4)
C(14)	1989 (4)	−443 (8)	3986 (4)
C(21)	3079 (5)	−574 (8)	1316 (4)
C(22)	3204 (4)	−1727 (8)	1806 (4)
C(23)	3464 (4)	1651 (8)	3872 (4)
C(24)	3308 (4)	2791 (8)	3379 (4)
C(*M*11)	1465 (6)	4489 (10)	1834 (6)
C(*M*12)	1378 (6)	2182 (13)	731 (4)
C(*M*13)	2071 (7)	−3008 (10)	3671 (6)
C(*M*14)	2196 (7)	−691 (12)	4743 (5)
C(*M*21)	2868 (7)	−766 (12)	555 (5)
C(*M*22)	3138 (6)	−3150 (12)	1609 (6)
C(*M*23)	3613 (6)	1829 (13)	4646 (5)
C(*M*24)	3224 (7)	4193 (12)	3618 (6)
C(151)	340 (5)	−1024 (12)	3549 (5)
C(152)	449 (6)	−746 (15)	4257 (6)
C(153)	468 (7)	−1801 (21)	4728 (7)
C(154)	410 (7)	−3120 (20)	4521 (8)
C(155)	321 (7)	−3398 (15)	3848 (9)
C(156)	270 (6)	−2334 (15)	3353 (7)
C(251)	4893 (5)	1922 (10)	3263 (5)
C(252)	4827 (5)	3281 (11)	3259 (5)
C(253)	5037 (6)	4082 (14)	3828 (6)
C(254)	5332 (6)	3446 (15)	4427 (6)
C(255)	5406 (6)	2050 (16)	4444 (6)
C(256)	5195 (6)	1274 (13)	3872 (7)
H(11)	41 (6)	2 (12)	259 (6)
H(12)	24 (7)	74 (12)	326 (6)
H(21)	468 (7)	161 (13)	241 (6)
H(22)	473 (7)	38 (12)	270 (7)
H(111)	117 (6)	506 (12)	210 (6)
H(112)	171 (7)	485 (14)	196 (7)
H(113)	129 (6)	458 (12)	143 (6)
H(121)	130 (6)	146 (12)	43 (6)
H(122)	101 (6)	301 (12)	58 (6)
H(123)	163 (7)	265 (14)	73 (7)
H(131)	204 (7)	−351 (13)	339 (6)
H(132)	180 (6)	−351 (12)	403 (6)
H(133)	248 (6)	−316 (13)	384 (6)
H(141)	222 (7)	−12 (13)	495 (6)
H(142)	259 (6)	−79 (14)	479 (7)
H(143)	179 (6)	−134 (12)	484 (6)
H(211)	321 (6)	−154 (12)	39 (6)
H(212)	250 (6)	−45 (14)	50 (7)
H(213)	293 (6)	5 (13)	39 (6)
H(221)	325 (6)	−342 (13)	125 (6)
H(222)	320 (6)	−369 (12)	203 (6)
H(223)	280 (6)	−315 (14)	145 (7)
H(231)	330 (6)	187 (15)	479 (7)
H(232)	391 (6)	263 (12)	464 (6)
H(233)	368 (6)	100 (12)	482 (6)
H(241)	321 (6)	480 (12)	334 (6)
H(242)	292 (6)	444 (13)	380 (6)
H(243)	355 (6)	443 (13)	388 (6)
H(152)	45 (6)	14 (12)	447 (6)
H(153)	49 (6)	−139 (13)	510 (6)
H(154)	37 (6)	−386 (13)	476 (6)
H(155)	29 (6)	−426 (12)	363 (6)
H(156)	35 (7)	−261 (13)	301 (6)
H(252)	466 (6)	356 (12)	281 (6)
H(253)	506 (6)	511 (12)	388 (6)
H(254)	554 (5)	430 (11)	477 (6)
H(255)	552 (6)	147 (12)	484 (6)
H(256)	529 (6)	39 (12)	383 (6)

anisotropic refinement the positions of the H atoms were allowed to vary, their parameters being included in the same matrices as the atoms to which they were bonded.

Refinement was terminated when the maximum shift in any parameter was $<0{\cdot}25\sigma$. A final difference synthesis showed maximum positive electron densities of 0·4 e Å^{-3}. *R* based on 3443 reflexions was 0·073 and $R' = (\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$ was 0·093. 3418 reflexions were included in the final cycle. Atomic coordinates are given in Table 1.*

Discussion

Bond lengths and angles are given in Table 2. A perspective drawing of the complex is given in Fig. 1 with the atomic labelling. Fig. 2 shows the packing viewed down *b*.

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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 33527 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Ni(1)—Ni(2)	3·654 (2)		
Ni(1)—N(11)	1·870 (7)	Ni(2)—N(21)	1·881 (6)
Ni(1)—N(12)	1·865 (6)	Ni(2)—N(22)	1·873 (7)
Ni(1)—N(13)	1·880 (7)	Ni(2)—N(23)	1·871 (6)
Ni(1)—N(14)	1·863 (6)	Ni(2)—N(24)	1·867 (6)
Ni(1)—N(15)	2·724 (9)	Ni(2)—N(25)	2·602 (10)
N(11)—O(11)	1·381 (8)	N(21)—O(21)	1·362 (8)
N(12)—O(12)	1·390 (8)	N(22)—O(22)	1·378 (8)
N(13)—O(13)	1·382 (8)	N(23)—O(23)	1·382 (8)
N(14)—O(14)	1·381 (8)	N(24)—O(24)	1·374 (8)
N(11) C(11)	1·292 (10)	N(21)—C(21)	1·303 (10)
N(12)—C(12)	1·303 (10)	N(22)—C(22)	1·294 (10)
N(13)—C(13)	1·277 (10)	N(23)—C(23)	1·301 (10)
N(14)—C(14)	1·287 (10)	N(24)—C(24)	1·294 (10)
C(11)—C(*M*11)	1·468 (13)	C(21)—C(*M*21)	1·506 (12)
C(12—C(*M*12)	1·503 (11)	C(22)—C(*M*22)	1·467 (14)
C(13)—C(*M*13)	1·484 (13)	C(23)—C(*M*23)	1·512 (13)
C(14)—C(*M*14)	1·506 (12)	C(24)—C(*M*24)	1·484 (14)
C(11)—C(12)	1·476 (11)	C(21)—C(22)	1·494 (11)
C(13)—C(14)	1·513 (11)	C(23)—C(24)	1·495 (12)
O(11)—B(11)	1·491 (11)	O(21)—B(21)	1·494 (12)
O(12)—B(12)	1·490 (13)	O(22)—B(22)	1·497 (12)
O(13)—B(12)	1·506 (12)	O(23)—B(22)	1·493 (13)
O(14)—B(11)	1·498 (12)	O(24)—B(21)	1·493 (11)
B(11)—F(111)	1·352 (11)	B(21)—F(211)	1·364 (11)
B(11)—F(112)	1·395 (13)	B(21)—F(212)	1·387 (13)
B(12)—F(121)	1·369 (12)	B(22)—F(221)	1·380 (11)
B(12)—F(122)	1·363 (14)	B(22)—F(222)	1·375 (15)
N(15)—C(151)	1·420 (14)	N(25)—C(251)	1·423 (13)
C(151)—C(152)	1·396 (14)	C(251)—C(252)	1·357 (13)
C(152)—C(153)	1·388 (19)	C(252)—C(253)	1·391 (14)
C(153)—C(154)	1·372 (21)	C(253)—C(254)	1·401 (16)
C(154)—C(155)	1·329 (20)	C(254)—C(255)	1·396 (18)
C(155)—C(156)	1·425 (19)	C(255)—C(256)	1·384 (16)
C(156)—C(151)	1·360 (16)	C(256)—C(251)	1·426 (14)
N(15)—H(11)	0·93 (12)	N(25)—H(21)	0·73 (12)
N(15)—H(12)	0·84 (12)	N(25)—H(22)	0·76 (12)
C(*M*11)—H(111)	1·00 (12)	C(*M*21)—H(211)	1·11 (12)
C(*M*11)—H(112)	0·65 (13)	C(*M*21)—H(212)	0·80 (12)
C(*M*11)—H(113)	0·84 (12)	C(*M*21) H(213)	0·88 (12)
C(*M*12)—H(121)	0·92 (12)	C(*M*22)—H(221)	0·79 (12)
C(*M*12)—H(122)	1·13 (12)	C(*M*22)—H(222)	0·98 (12)
C(*M*12)—H(123)	0·69 (13)	C(*M*22)—H(223)	0·72 (12)
C(*M*13)—H(131)	0·74 (12)	C(*M*23)—H(231)	0·72 (12)
C(*M*13)—H(132)	1·05 (12)	C(*M*23)—H(232)	1·00 (12)
C(*M*13)—H(133)	0·88 (12)	C(*M*23)—H(233)	0·90 (12)
C(*M*14)—H(141)	0·69 (12)	C(*M*24)—H(241)	0·81 (12)
C(*M*14)—H(142)	0·79 (12)	C(*M*24)—H(242)	0·79 (12)
C(*M*14)—H(143)	1·07 (12)	C(*M*24)—H(243)	0·82 (12)
C(152)—H(152)	0·97 (12)	C(252)—H(252)	0·94 (1.1)
C(153)—H(153)	0·83 (12)	C(253)—H(253)	1·03 (12)
C(154)—H(154)	0·88 (12)	C(254)—H(254)	1·13 (12)
C(155)—H(155)	0·95 (12)	C(255)—H(255)	0·98 (11)
C(156)—H(156)	0·75 (12)	C(256)—H(256)	0·90 (12)
N(11)—Ni(1)—N(12)	81·3 (3)	N(21)—Ni(2)—N(22)	82·0 (3)
N(13)—Ni(1)—N(14)	82·0 (3)	N(23)—Ni(2)—N(24)	82·3 (3)
N(11)—Ni(1)—N(14)	97·7 (3)	N(21)—Ni(2)—N(24)	97·0 (3)
N(12)—Ni(1)—N(13)	98·1 (3)	N(22)—Ni(2)—N(23)	97·4 (3)
N(11)—Ni(1)—N(13)	173·5 (3)	N(21)—Ni(2)—N(23)	172·9 (3)
N(12)—Ni(1)—N(14)	172·0 (3)	N(22)—Ni(2)—N(24)	170·2 (3)
N(15)—Ni(1)—N(11)	101·9 (3)	N(25)—Ni(2)—N(21)	102·2 (2)
N(15)—Ni(1)—N(12)	102·0 (3)	N(25)—Ni(2)—N(22)	102·8 (3)
N(15)—Ni(1)—N(13)	84·6 (3)	N(25)—Ni(2)—N(23)	84·9 (3)
N(15)—Ni(1)—N(14)	86·0 (3)	N(25)—Ni(2)—N(24)	87·0 (3)
Ni(2)—Ni(1)—N(11)	95·5 (2)	Ni(1)—Ni(2)—N(21)	86·9 (2)
Ni(2)—Ni(1)—N(12)	86·1 (2)	Ni(1)—Ni(2)—N(22)	93·3 (2)
Ni(2)—Ni(1)—N(13)	78·0 (2)	Ni(1)—Ni(2)—N(23)	86·1 (2)
Ni(2)—Ni(1)—N(14)	86·1 (2)	Ni(1)—Ni(2)—N(24)	76·9 (2)
Ni(2)—Ni(1)—N(15)	161·7 (2)	Ni(1)—Ni(2)—N(25)	162·4 (2)
Ni(1)—N(11)—O(11)	124·0 (5)	Ni(2)—N(21)—O(21)	124·3 (5)
Ni(1)—N(11)—C(11)	118·5 (6)	Ni(2)—N(21)—C(21)	116·0 (5)
O(11)—N(11)—C(11)	116·7 (6)	O(21)—N(21)—C(21)	119·4 (6)
Ni(1)—N(12)—O(12)	123·4 (5)	Ni(2)—N(22)—O(22)	124·2 (5)
Ni(1)—N(12)—C(12)	116·8 (5)	Ni(2)—O(22)—C(22)	118·2 (6)
O(12)—N(12)—C(12)	119·3 (6)	O(22)—N(22)—C(22)	116·9 (7)
Ni(1)—N(13)—O(13)	124·0 (5)	Ni(2)—N(23)—O(23)	124·3 (5)
Ni(1)—N(13)—C(13)	118·0 (6)	Ni(2)—N(23)—C(23)	116·6 (5)
O(13)—N(13)—C(13)	118·1 (7)	O(23)—N(23)—C(23)	119·1 (6)
Ni(1)—N(14)—O(14)	124·7 (5)	Ni(2)—N(24)—O(24)	125·1 (5)
Ni(1)—N(14)—C(14)	116·8 (5)	Ni(2)—N(24)—C(24)	117·2 (6)
O(14)—N(14)—C(14)	118·4 (6)	O(24)—N(24)—C(24)	117·7 (7)
Ni(1)—N(15)—C(151)	114·7 (6)	Ni(2)—N(25)—C(251)	116·2 (6)
N(11)—O(11)—B(11)	116·7 (6)	N(21)—O(21)—B(21)	117·4 (6)
N(12)—O(12)—B(12)	115·8 (6)	N(22)—O(22)—B(22)	114·2 (6)
N(13)—O(13)—B(12)	117·0 (7)	N(23)—O(23)—B(22)	117·4 (6)
N(14)—O(14)—B(11)	115·9 (6)	N(24)—O(24)—B(21)	115·8 (6)
O(11)—B(11)—F(111)	106·3 (8)	O(21)—B(21)—F(211)	105·6 (7)
O(11)—B(11)—F(112)	109·1 (8)	O(21)—B(21)—F(212)	109·0 (9)
O(14)—B(11)—F(111)	107·1 (8)	O(24)—B(21)—F(211)	106·4 (8)
O(14)—B(11)—F(112)	107·7 (8)	O(24)—B(21)—F(212)	109·2 (7)
O(11)—B(11)—O(14)	112·4 (8)	O(21)—B(21)—O(24)	113·0 (7)
F(111)—B(11)—F(112)	114·3 (9)	F(211)—B(21)—F(212)	113·8 (8)
O(12)—B(12)—F(121)	104·7 (8)	O(22)—B(22)—F(221)	104·8 (8)
O(12)—B(12)—F(122)	110·2 (9)	O(22)—B(22)—F(222)	109·9 (9)
O(13)—B(12)—F(121)	104·7 (8)	O(23)—B(22)—F(221)	105·3 (9)
O(13)—B(12)—F(122)	110·6 (9)	O(23)—B(22)—F(222)	110·0 (8)
O(12)—B(12)—O(13)	111·9 (8)	O(22)—B(22)—O(23)	112·3 (9)
F(121)—B(12)—F(122)	114·5 (9)	F(221)—B(22)—F(222)	113·4 (9)
N(11)—C(11)—C(12)	110·4 (7)	N(21)—C(21)—C(22)	113·2 (7)
N(11)—C(11)—C(*M*11)	125·3 (7)	N(21)—C(21)—C(*M*21)	124·2 (8)
C(12)—C(11)—C(*M*11)	124·3 (7)	C(22)—C(21)—C(*M*21)	122·6 (8)
N(12)—C(12)—C(11)	112·9 (6)	N(22)—C(22)—C(21)	110·6 (7)
N(12)—C(12)—C(*M*12)	123·8 (8)	N(22)—C(22)—C(*M*22)	124·7 (8)
C(11)—C(12)—C(*M*12)	123·2 (8)	C(21)—C(22)—C(*M*22)	124·7 (8)
N(13)—C(13)—C(14)	110·4 (7)	N(23)—C(23)—C(24)	111·8 (7)
N(13)—C(13)—C(*M*13)	126·8 (8)	N(23)—C(23)—C(*M*23)	124·3 (8)
C(14)—C(13)—C(*M*13)	122·8 (7)	C(24)—C(23)—C(*M*23)	123·6 (8)
N(14)—C(14)—C(13)	112·7 (6)	N(24)—C(24)—C(23)	111·7 (7)
N(14)—C(14)—C(*M*14)	126·1 (8)	N(24)—C(24)—C(*M*24)	125·9 (8)
C(13)—C(14)—C(*M*14)	121·2 (7)	C(23)—C(24)—C(*M*24)	122·4 (4)
N(15)—C(151)—C(152)	119·7 (11)	N(25)—C(251)—C(252)	121·4 (9)
N(15)—C(151) C(156)	122·4 (10)	N(25) C(251)—C(256)	119·4 (9)
C(156)—C(151)—C(152)	117·7 (11)	C(256)—C(251)—C(252)	119·2 (10)
C(151)—C(152)—C(153)	119·3 (13)	C(251)—C(252)—C(253)	122·9 (10)
C(152)—C(153)—C(154)	122·2 (13)	C(252)—C(253)—C(254)	118·0 (11)
C(153)—C(154)—C(155)	119·0 (12)	C(253)—C(254)—C(255)	120·3 (11)
C(154)—C(155)—C(156)	120·1 (14)	C(254)—C(255)—C(256)	120·7 (12)
C(155)—C(156)—C(151)	121·6 (11)	C(255)—C(256)—C(251)	119·0 (11)
Ni(1)—N(15)—H(11)	65 (10)	Ni(2)—N(25)—H(21)	105 (10)
Ni(1)—N(15)—H(12)	102 (9)	Ni(2)—N(25)—H(22)	91 (11)
C(151)—N(15)—H(11)	131 (8)	C(251)—N(25)—H(21)	99 (10)
C(151)—N(15)—H(12)	107 (9)	C(251)—N(25)—H(22)	116 (10)
H(11)—N(15)—H(12)	122 (12)	H(21)—N(25)—H(22)	130 (14)
C(11)—C(*M*11)—H(111)	115 (7)	C(21)—C(*M*21)—H(211)	105 (6)
C(11)—C(*M*11)—H(112)	118 (13)	C(21)—C(*M*21)—H(212)	104 (9)
C(11)—C(*M*11)—H(113)	108 (9)	C(21)—C(*M*21)—H(213)	102 (8)
H(111)—C(*M*11)—H(112)	88 (13)	H(211)—C(*M*21)—H(212)	146 (11)
H(111)—C(*M*11)—H(113)	102 (10)	H(211)—C(*M*21)—H(213)	115 (11)
H(112)—C(*M*11)—H(113)	123 (15)	H(212)—C(*M*21)—H(213)	75 (11)
C(12)—C(*M*12)—H(121)	119 (7)	C(22)—C(*M*22)—H(221)	121 (9)
C(12)—C(*M*12)—H(122)	111 (6)	C(22)—C(*M*22)—H(222)	108 (7)
C(12)—C(*M*12)—H(123)	98 (11)	C(22)—C(*M*22)—H(223)	100 (7)
H(121)—C(*M*12)—H(122)	109 (9)	H(221)—C(*M*22)—H(222)	122 (11)
H(121)—C(*M*12)—H(123)	126 (14)	H(221)—C(*M*22)—H(223)	88 (12)
H(122)—C(*M*12)—H(123)	89 (12)	H(222)—C(*M*22)—H(223)	114 (10)
C(13)—C(*M*13)—H(131)	116 (10)	C(23)—C(*M*23)—H(231)	107 (11)
C(13)—C(*M*13)—H(132)	122 (6)	C(23)—C(*M*23)—H(232)	98 (6)
C(13)—C(*M*13)—H(133)	114 (8)	C(23)—C(*M*23)—H(233)	106 (7)
H(131)—C(*M*13)—H(132)	99 (11)	H(231)—C(*M*23)—H(232)	121 (14)
H(131)—C(*M*13)—H(133)	99 (13)	H(231)—C(*M*23)—H(233)	90 (13)
H(132) C(*M*13)—H(133)	103 (10)	H(232)—C(*M*23)—H(233)	132 (10)
C(14)—C(*M*14)—H(141)	115 (11)	C(24)—C(*M*24)—H(241)	119 (9)
C(14)—C(*M*14)—H(142)	108 (10)	C(24)—C(*M*24)—H(242)	124 (10)
C(14)—C(*M*14)—H(143)	97 (6)	C(24)—C(*M*24)—H(243)	111 (10)
H(141)—C(*M*14)—H(142)	92 (14)	H(241)—C(*M*24)—H(242)	95 (12)
H(141)—C(*M*14)—H(143)	114 (13)	H(241)—C(*M*24)—H(243)	101 (11)
H(142)—C(*M*14)—H(143)	132 (12)	H(242)—C(*M*24)—H(243)	104 (11)
C(151)—C(152)—H(152)	126 (7)	C(251)—C(252)—H(252)	109 (7)
C(156)—C(152)—H(152)	114 (7)	C(256)—C(252)—H(252)	128 (7)
C(152)—C(153)—H(153)	101 (9)	C(252)—C(253)—H(253)	131 (7)
C(154)—C(153)—H(153)	136 (9)	C(254)—C(253)—H(253)	110 (7)
C(153)—C(154)—H(154)	131 (8)	C(253)—C(254)—H(254)	104 (6)
C(155)—C(154)—H(154)	109 (8)	C(255)—C(254)—H(254)	134 (6)
C(154)—C(155)—H(155)	128 (8)	C(254)—C(255)—H(255)	128 (7)
C(156)—C(155)—H(155)	111 (8)	C(256)—C(255)—H(255)	110 (7)
C(155)—C(156)—H(156)	125 (11)	C(255)—C(256)—H(256)	116 (8)
C(151)—C(156)—H(156)	109 (11)	C(251)—C(256)—H(256)	124 (8)

The dimeric nature of the planar parent Ni(dmg-$BF_2)_2$, with a *cis* conformation of the BF_2 groups (Stephens & Vagg, 1977*a*), is retained upon reaction with the base, which coordinates to each Ni in an axial position forming an irregular square pyramid. The two formula units in the dimer are non-equivalent. The eight equatorial Ni—N bonds [average 1·871 (7) Å] are

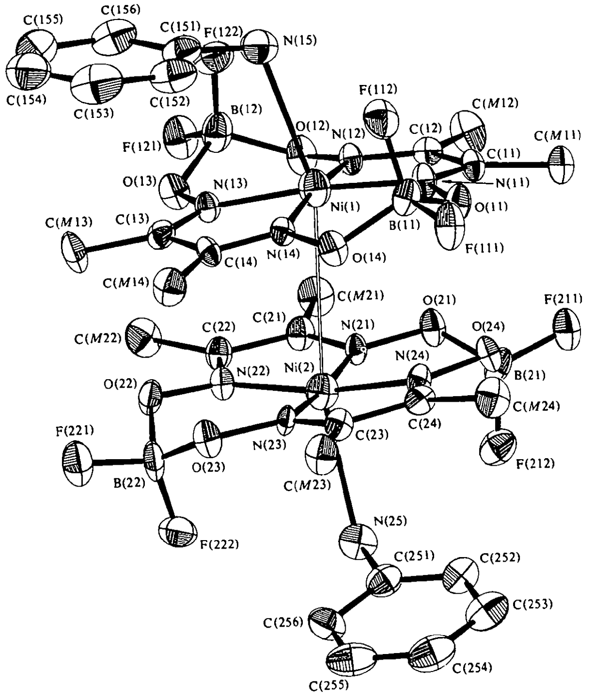

Fig. 1. Perspective drawing of the dimer (Johnson, 1965) and the labelling of the atoms. H atoms have been excluded for clarity. Thermal ellipsoids are scaled to include 35% probability.

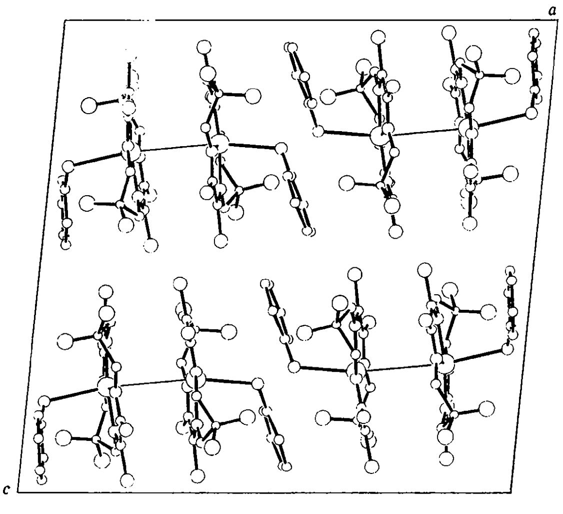

Fig. 2. The packing of the molecules in the crystal.

similar to those found in the parent and other low-spin Ni^{II} glyoximates (Stephens & Vagg, 1977*a*), and are 0·2 Å shorter than those of a comparable high-spin complex (Stephens & Vagg, 1977*b*). The two aniline Ni–N lengths [2·724 (9) and 2·602 (10) Å] differ significantly. The Ni atoms are displaced 0·118 and 0·138 Å out of the equatorial coordination planes (Table 3, planes 1 and 2 respectively) towards the aniline N atoms. This results in a slight angular distortion of the macrocyclic rings from the planarity found in the parent structure, although the bond lengths are unchanged.

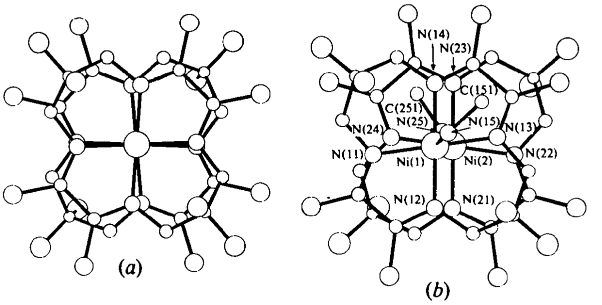

Fig. 3. Relative orientations of the macrocycles in the dimeric compounds projected perpendicular to the equatorial N atom planes. (*a*) $Ni(dmgBF_2)_2$; taken from Stephens & Vagg (1977*a*). (*b*) This work; for clarity the phenyl rings of the aniline molecules are not included.

The four five-membered coordination rings are planar (Table 3, planes 3–6) and the N atoms are trigonally planar (Table 3, planes 7–14). The two equatorial coordination planes are parallel (Table 3, planes 1 and 2 intersect at 0·7°) although their relative orientation is different from that of $Ni(dmgBF_2)_2$. This change involves both a rotation of 6·7° and a translation of 0·56 Å perpendicular to the Ni–Ni direction. The Ni–Ni separation in the adduct is thus increased 0·44 Å to 3·654 (2) Å. A comparison of these two orientations is shown in Fig. 3. As a result the molecular structure changes from the *M–M* to the *M–L–M* stacking arrangement (Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977). This effect might be expected with the increase in electron density on the Ni atoms, and consequent increase in repulsive forces, that results from the base coordination (Endres *et al.*, 1977).

Although the vertical separation between the Ni atoms is 3·60 Å the close packing of the two macrocycles in the dimer is retained. Intermolecular contact distances are comparable with those found in the parent structure (Stephens & Vagg, 1977*a*). In particular the shorter C···O contacts (Table 4) are similar to those in the parent, which average 3·16 (2) Å. It has been suggested (Endres *et al.*, 1977) that close packing of the organic ligands in these types of complexes occurs at a spacing of about 3·2 Å.

To some extent steric interactions may account for the unusual nature of the long $Ni-N_{aniline}$ bonds. Ni(1)–N(15) and Ni(2)–N(25) are each inclined at 78·9° to the equatorial coordination planes. The axial F atoms would hinder approach of the base, resulting in this unusual directional character. The N···F separations (Table 4), average 3·06 (1) Å, would correspond to closest approach distances for these atoms.

Table 3. *Least-squares planes and their equations given by* $lX' + mY' + nZ' - p = 0$

X', Y' and Z' are orthogonal coordinates related to the atomic coordinates X, Y and Z by $X' = X \sin\beta$, $Y' = Y$ and $Z' = Z + X\cos\beta$. Deviations (Å) of relevant atoms from the planes are given in square brackets.

	l	*m*	*n*	*p*
Plane (1): N(11)—N(14) [N(11), N(13) −0·011; N(12), N(14) 0·011; Ni(1) −0·118; O(11) 0·10; O(12) 0·12; O(13) 0·01; O(14) 0·13; C(11), C(12) 0·16; C(13) 0·03; C(14) 0·08; C(*M*11) 0·38; C(*M*12) 0·34; C(*M*13) 0·07; C(*M*14) 0·19]	0·9755	0·1144	−0·1878	2·3948
Plane (2): N(21)—N(24) [N(21), N(23) 0·022; N(22), N(24) −0·022; Ni(2) 0·138; O(21) −0·03; O(22), C(22) −0·18; O(23) 0·01; O(24) −0·10; C(21) −0·14; C(23) −0·04; C(24) −0·06; C(*M*21) −0·31; C(*M*22) −0·39; C(*M*23) 0·004; C(*M*24) −0·17]	0·9780	0·1032	−0·1815	5·7866
Plane (3): Ni(1), N(11), N(12), C(11), C(12) [Ni(1) 0·017; N(11) −0·022; N(12) −0·016; C(11) 0·015; C(12) 0·005]	0·9934	0·0467	−0·1046	2·6864
Plane (4): Ni(1), N(13), N(14), C(13), C(14) [Ni(1) −0·013; N(13) 0·022; N(14), C(14) 0·006; C(13) −0·021]	0·9588	0·1450	−0·2445	1·9736
Plane (5): Ni(2), N(21), N(22), C(21), C(22) [Ni(2), C(22) −0·012; N(21) 0·010; N(22) 0·016; C(21) −0·002]	0·9666	0·0132	−0·2561	5·4874
Plane (6): Ni(2), N(23), N(24), C(23), C(24) [Ni(2) 0·020; N(23) −0·020; N(24) −0·022; C(23) 0·010; C(24) 0·013]	0·9773	0·1602	−0·1388	6·1159
Plane (7): N(11), O(11), C(11), Ni(1) [N(11) −0·055; O(11), C(11) 0·020; Ni(1) 0·015]	0·9892	0·0251	−0·1445	2·4598
Plane (8): N(12), O(12), C(12), Ni(1) [N(12) −0·045; O(12), C(12) 0·016; Ni(1) 0·012]	0·9921	0·0876	−0·0903	2·7878
Plane (9): N(13), O(13), C(13), Ni(1) [N(13) 0·005; O(13), C(13) −0·002; Ni(1) −0·001]	0·9643	0·1649	−0·2074	2·1795
Plane (10): N(14), O(14), C(14), Ni(1) [N(14) −0·025; O(14), C(14) 0·009; Ni(1) 0·007]	0·9569	0·1021	−0·2720	1·7801
Plane (11): N(21), O(21), C(21), Ni(2) [N(21) 0·036; O(21) −0·014; C(21) −0·013; Ni(2) −0·010]	0·9623	0·0507	−0·2671	5·4296
Plane (12): N(22), O(22), C(22), Ni(2) [N(22) 0·055; O(22), C(22) −0·020; Ni(2) −0·015]	0·9777	−0·0165	−0·2093	5·7510
Plane (13): N(23), O(23), C(23), Ni(2) [N(23) −0·004; O(23), C(23), Ni(2) 0·001]	0·9842	0·1288	−0·1215	6·2386
Plane (14): N(24), O(24), C(24), Ni(2) [N(24) 0·001; O(24), C(24) −0·004; Ni(2) 0·0003]	0·9657	0·1896	−0·1774	5·9072
Plane (15): C(151)—C(156) [C(151) 0·0002; C(152) −0·014; C(153), C(156) 0·014; C(154) 0·001; C(155) −0·015; N(15) −0·108]	−0·9887	0·0566	0·1387	0·2133
Plane (16): C(251)—C(256) [C(251) −0·003; C(252) 0·002; C(253) −0·0006; C(254) 0·0003; C(255) −0·001; C(256) 0·003; N(25) −0·062]	0·8984	0·0927	−0·4293	6·7331
Plane (17): N(13), N(14), O(13), O(14), C(13), C(14), C(*M*13), C(*M*14) [N(13) −0·013; N(14) −0·053; O(13) 0·045; O(14) 0·034; C(13) −0·024; C(14) −0·012; C(*M*13) −0·011; C(*M*14) 0·033; Ni(1) −0·102]	0·9661	0·1182	−0·2293	2·1438
Plane (18): N(23), N(24), O(23), O(24), C(23), C(24), C(*M*23) C(*M*24) [N(23), C(24) 0·012; N(24) 0·038; O(23) −0·041; O(24), C(23) −0·008; C(*M*23) 0·040; C(*M*24) −0·045; Ni(2) 0·132]	0·9734	0·1394	−0·1819	5·7798

Table 4. *Intermolecular contact distances below* 3·30 Å

N(15)···F(112)	3·077 (12) Å	O(21)···C(12)	3·254 (10) Å
N(15)···F(122)	3·062 (12)	O(22)···C(*M*13)	3·299 (15)
N(25)···F(212)	3·050 (11)	O(24)···C(11)	3·206 (10)
N(25)···F(222)	3·065 (11)	C(151)···C(13)	3·292 (13)
O(12)···C(21)	3·154 (11)	C(152)···C(14)	3·223 (14)
O(12)···C(*M*21)	3·299 (15)	C(251)···N(23)	3·250 (11)
O(13)···C(22)	3·232 (11)	C(251)···C(23)	3·240 (13)
O(14)···C(23)	3·237 (11)	C(252)···C(24)	3·140 (14)

An alternative bonding description, involving only N—H···F bonding with no Ni—N$_{\text{aniline}}$ interaction can be discounted after a consideration of both the distortions in the coordination geometry of the Ni atoms, and the refined positions of the H atoms. There is no H-bonding apparent in the structure.

The O—B—F angles [average, 107·5 (8)°] are significantly less than those of O—B—O [average, 112·4 (8)°] and F—B—F [average, 114·0 (9)°]. The average N—O—B angle of 116·3 (6)° compares with 114 (2)° in the parent.

The phenyl groups are planar (Table 3, planes 15 and 16), with the N atoms slightly out of these planes, and their orientation relative to the glyoxime moieties is similar to that found in two substituted-aniline adducts of cobaloxime (Palenik, Sullivan & Naik, 1975) where a π-type interaction between the aniline and dmg rings has been suggested. The planes concerned are much closer to parallel than in the Co structures (Table 3, planes 15 and 17 intersect at 11·4°, 16 and 18 at 15·1°) and the closest approach of each pair is 3·00 and 2·90 Å at C(151) and C(251) respectively. Close contacts are given in Table 4.

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The Crystal and Molecular Structure of Tetramethylammonium 1-η-Cyclopentadienyl-1-ferra-2-carbaundecaborate

BY V. ŠUBRTOVÁ AND A. LÍNEK

Institute of Solid State Physics, Czechoslovak Academy of Sciences, 162 53 *Praha* 6, *Czechslovakia*

AND J. HAŠEK

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 *Praha* 6, *Czechoslovakia*

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$[N(CH_3)_4]^+[\eta\text{-}(C_5H_5)FeCB_9H_{10}]^-$ is orthorhombic, space group $P2_12_12_1$, with a = 10·092 (5), b = 11·116 (6), c = 15·377 (5) Å and Z = 4. The structure was solved by the heavy-atom method and refined to R_w = 0·053 for 1760 counter reflections. The new ferracarbaborate anion was found to be the eleven-vertex polyhedron, where the metal atom occupies the vertex of highest coordination number and is also coordinated to the cyclopentadienyl ring. The carbon atom occupies the vertex of lowest coordination.

Introduction

The present study reports the results of an X-ray investigation of a tetramethylammonium salt of a new ferracarbaborate complex with eleven non-hydrogen atoms in the metallocarbaborate skeleton. Crystals were prepared at the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences, at Řež near Prague.

Experimental

Preliminary data were obtained from oscillation and Weissenberg photographs (Co $K\alpha$ radiation, λ = 1·790 Å). Systematic absences correspond to the space group $P2_12_12_1$. Refined cell parameters were determined by the least-squares method from twenty reflections centred on the diffractometer. Crystal data are summarized in Table 1.

The intensities were collected at room temperature with a fragile crystal (0·1 × 0·2 × 0·1 mm) mounted on a four-circle Syntex $P2_1$ automatic diffractometer (Mo $K\alpha$ radiation, graphite monochromator). 1760 independent reflections were measured in the $\omega/2\theta$ scan mode to 2θ = 50°. The scan speed varied from 0·95 to 29·3° min^{-1} and was determined from a rapid prescan. The scanning interval was from 1° below $K\alpha_1$ to 1° above $K\alpha_2$ of the Mo $K\alpha$ doublet. 363 reflections were considered to be unobserved according to the criterion $I < 1{\cdot}96\sigma(I)$ where $I = [TC - (B_1 + B_2)]R$ and $\sigma(I) =$

Table 1. *Crystal data*

$[N(CH_3)_4]^+[(C_5H_5)FeCB_9H_{10}]^-$	Orthorhombic, $P2_12_12_1$
a = 10·092 (5) Å	Z = 4
b = 11·116 (6)	M_r = 314·6
c = 15·377 (5)	D_m = 1·210 g cm^{-3}
V = 1724·8 Å^3	D_c = 1·207