

A second monoclinic polymorph of {2,6-bis[(2,4,5-trifluorophenyl)iminomethyl]pyridine- κ^3N,N',N'' }dichloridonickel(II)

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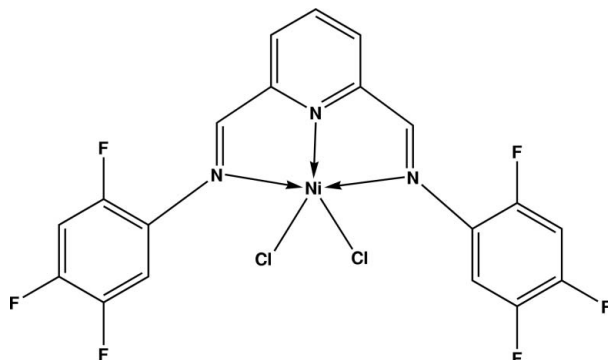
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.025; wR factor = 0.058; data-to-parameter ratio = 12.3.

The asymmetric unit of the title compound, $[\text{NiCl}_2(\text{C}_{19}\text{H}_9\text{F}_6\text{N}_3)]$, contains one half-molecule residing on a crystallographic twofold rotation axis. The title compound crystallizes in space group $C2/c$ while the previously reported polymorph was reported in $P2_1/c$ [Baldovino-Pantaleón *et al.* (2006). *Adv. Synth. Catal.* **348**, 236–242]. The Ni^{2+} ion exhibits a pentacoordinate distorted trigonal–bipyramidal NiCl_2N_3 geometry, with two Cl atoms in the equatorial plane. In the crystal, molecules are linked by intermolecular $\text{C}-\text{F}\cdots\pi$ [$\text{F}\cdots\text{centroid} = 2.9676$ (14) Å] interactions.

Related literature

For related studies, see: Baldovino-Pantaleón *et al.* (2005, 2006); Morales-Morales (2008); Serrano-Becerra & Morales-Morales (2009). For catalysis reactions, see: Gómez-Benítez *et al.* (2006). For the previously reported polymorph, see: Baldovino-Pantaleón *et al.* (2006).



Experimental

Crystal data

$[\text{NiCl}_2(\text{C}_{19}\text{H}_9\text{F}_6\text{N}_3)]$
 $M_r = 522.90$
 Monoclinic, $C2/c$
 $a = 18.0947$ (13) Å
 $b = 8.8967$ (6) Å
 $c = 12.1638$ (9) Å
 $\beta = 101.421$ (2)°

$V = 1919.4$ (2) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.36$ mm⁻¹
 $T = 298$ K
 $0.32 \times 0.16 \times 0.06$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 Absorption correction: analytical (*SHELXTL*; Sheldrick, 2008)
 $T_{\min} = 0.740$, $T_{\max} = 0.921$

7821 measured reflections
 1751 independent reflections
 1482 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.058$
 $S = 0.96$
 1751 reflections

142 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.23$ e Å⁻³
 $\Delta\rho_{\min} = -0.20$ e Å⁻³

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2491).

References

- Baldovino-Pantaleón, O., Hernández-Ortega, S. & Morales-Morales, D. (2005). *Inorg. Chem. Commun.* **8**, 955–959.
 Baldovino-Pantaleón, O., Hernández-Ortega, S. & Morales-Morales, D. (2006). *Adv. Synth. Catal.* **348**, 236–242.
 Bruker (2007). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Gómez-Benítez, V., Baldovino-Pantaleón, O., Herrera-Alvarez, C., Toscano, R. A. & Morales-Morales, D. (2006). *Tetrahedron Lett.* **47**, 5059–5062.
 Morales-Morales, D. (2008). *Mini-Rev. Org. Chem.* **5**, 141–152.
 Serrano-Becerra, J. M. & Morales-Morales, D. (2009). *Curr. Org. Synth.* **6**, 169–192.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supporting information

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A second monoclinic polymorph of {2,6-bis[(2,4,5-trifluorophenyl)imino-methyl]pyridine- κ^3N,N',N'' }dichloridonickel(II)

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S1. Comment

For the last decade our research group has focused on the design, synthesis and use of pincer-type ligands and their transition metal complexes for novel organic transformations (Morales-Morales 2008; Serrano-Becerra & Morales-Morales, 2009). The selection of these ligands has been done on the basis of the robustness that they confer to the transition metal complexes they form (Baldovino-Pantaleón, *et al.*, 2005, 2006). In recent years this kind of complexes have gained more interest particularly those derived from Ni, due to the importance that cross-coupling reactions have gained in important organic transformations of potential industrial relevance and the potential application of the nickel derivatives for the same sort of process regularly catalized by analogous palladium derivatives, but using a far more cheaper metal (Gómez-Benítez *et al.*, 2006). The title compound is a polymorphous of a compound described previously (Baldovino-Pantaleón, *et al.*, 2006).

The molecular structure of I is shown in figure 1 with the numbering scheme. In comparison, compound II described previously (Baldovino-Pantaleón, *et al.*, 2006), was crystallized in a monoclinic (P 2₁/c), while compound I, crystallizes in space group C 2/c. The asymmetric unit consists of a half molecule with Ni—N1—C4—H4 in a special position (1/2, y, 1/4), and by two fold axis the complete molecule is generated. The Ni atom is found in a pentacoordinated distorted bipyramidal geometry with the two chlorides occupying the equatorial positions. While the fragment N1—Ni—N2—N2A is planar, the pyridine ring is slightly rotated by 5.4 (1)°. The 2,4,5-trifluorophenyl ring is not coplanar and is forming a dihedral angle of 39.41 (5)° with the coordination metallic center, while in II, the fluorophenyl rings have dihedral angles of 14.4 (2)° and 13.4 (2)° with the coordination metallic center. The bond distances Ni—N(imino) in I are slightly shorter than in II. In absence of classic acceptor-donor H atom, the weak interactions become very important stabilizing the crystal structure. The molecules in the crystal structure are linked by C—H—F—C, C—H— π , C—F— π and C—F—F—C intermolecular interactions (Table 1).

S2. Experimental

A solution of the ligand {C₅H₃N-2,6-(CH=N—C₆H₂-2,4,5-F₃)₂} (120 mg, 0.33 mmol) in anhydrous CH₂Cl₂ (10 ml) was added to a stirred solution of NiCl₂.6 H₂O(0.078 g, 0.33 mmol) in absolute methanol (10 ml). The resulting green solution was stirred at room temperature for 2 h. After this time a red suspension is noted and the solvent evaporated under vacuum. The product was purified by recrystallization from MeOH; the resulting precipitated was filtered and washed with hexane (3 X 5 ml) and dried under vacuum. Crystals suitable for single-crystal X-ray diffraction studies were obtained from a dichloromethane/ methanol (4:1) solution. A red solid was obtained; yield: 142 mg (88%); mp: 240°C

S3. Refinement

H atoms were included in calculated positions ($C-H = 0.93 \text{ \AA}$), and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the carrier atom.

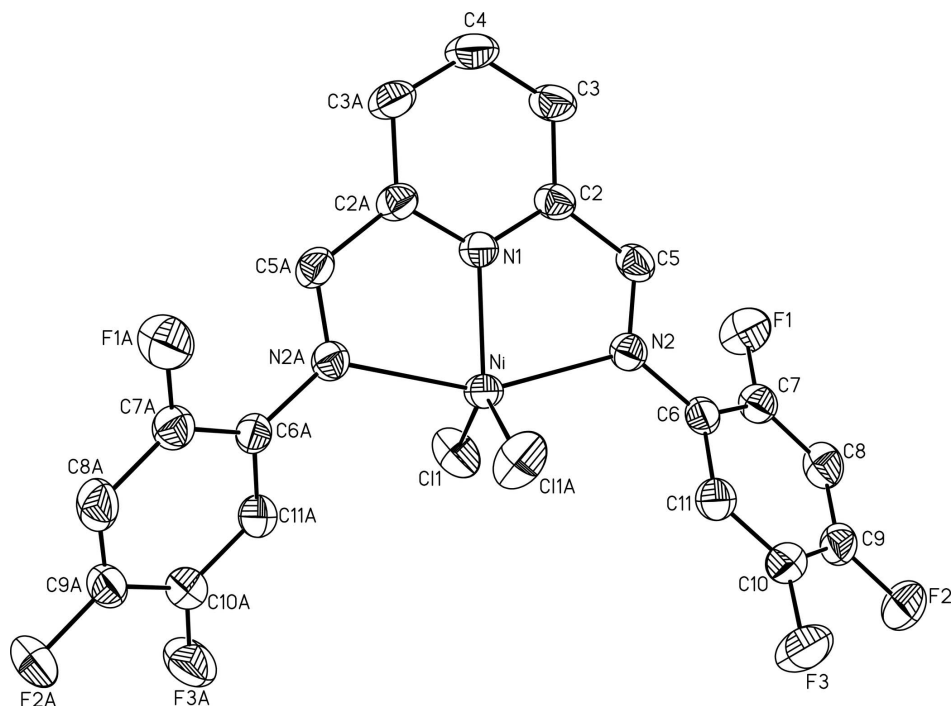


Figure 1

The molecular structure of I with the numbering scheme. Displacement ellipsoids are shown at the 40% probability level. H atoms have been omitted for clarity.

{2,6-Bis[(2,4,5-trifluorophenyl)iminomethyl]pyridine- κ^3N,N',N'' }dichloridonickel(II)

Crystal data

$[\text{NiCl}_2(\text{C}_{19}\text{H}_9\text{F}_6\text{N}_3)]$

$M_r = 522.90$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 18.0947 (13) \text{ \AA}$

$b = 8.8967 (6) \text{ \AA}$

$c = 12.1638 (9) \text{ \AA}$

$\beta = 101.421 (2)^\circ$

$V = 1919.4 (2) \text{ \AA}^3$

$Z = 4$

$F(000) = 1040$

$D_x = 1.810 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 5009 reflections

$\theta = 2.6\text{--}32.1^\circ$

$\mu = 1.36 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Prism, red

$0.32 \times 0.16 \times 0.06 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: $0.83 \text{ pixels mm}^{-1}$

ω scans

Absorption correction: analytical
(*SHELXTL*; Sheldrick, 2008)

$T_{\text{min}} = 0.740$, $T_{\text{max}} = 0.921$

7821 measured reflections

1751 independent reflections

1482 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 25.3^\circ$, $\theta_{\min} = 2.3^\circ$
 $h = -21 \rightarrow 21$

$k = -10 \rightarrow 10$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.058$
 $S = 0.96$
 1751 reflections
 142 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.034P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.5000	0.68998 (3)	0.2500	0.03615 (12)
Cl1	0.42526 (3)	0.79023 (6)	0.35781 (4)	0.06007 (17)
F1	0.62550 (7)	0.60471 (13)	0.63576 (9)	0.0642 (3)
F2	0.75608 (7)	1.06173 (13)	0.66763 (10)	0.0688 (4)
F3	0.72148 (8)	1.09768 (14)	0.44569 (11)	0.0767 (4)
N1	0.5000	0.4707 (2)	0.2500	0.0352 (5)
N2	0.58620 (8)	0.63599 (16)	0.39784 (11)	0.0372 (3)
C2	0.54313 (10)	0.39674 (18)	0.33462 (14)	0.0384 (4)
C3	0.54303 (12)	0.2412 (2)	0.33833 (16)	0.0505 (5)
H3	0.5714	0.1902	0.3991	0.061*
C4	0.5000	0.1634 (3)	0.2500	0.0586 (8)
H4	0.5000	0.0588	0.2500	0.070*
C5	0.58923 (10)	0.4948 (2)	0.41731 (13)	0.0399 (4)
H5	0.6196	0.4559	0.4817	0.048*
C6	0.63018 (9)	0.7410 (2)	0.47162 (14)	0.0376 (4)
C7	0.64917 (10)	0.7265 (2)	0.58667 (15)	0.0428 (4)
C8	0.69027 (11)	0.8327 (2)	0.65465 (16)	0.0513 (5)
H8	0.7015	0.8207	0.7321	0.062*
C9	0.71419 (10)	0.9570 (2)	0.60497 (16)	0.0478 (5)
C10	0.69631 (11)	0.9745 (2)	0.49109 (16)	0.0483 (5)
C11	0.65417 (10)	0.8698 (2)	0.42393 (15)	0.0461 (5)
H11	0.6416	0.8847	0.3468	0.055*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0457 (2)	0.02916 (18)	0.03209 (19)	0.000	0.00412 (14)	0.000
Cl1	0.0713 (4)	0.0718 (4)	0.0386 (3)	0.0258 (3)	0.0145 (2)	0.0021 (2)
F1	0.0917 (9)	0.0633 (8)	0.0368 (6)	-0.0145 (7)	0.0106 (6)	0.0031 (5)
F2	0.0692 (8)	0.0631 (8)	0.0648 (8)	-0.0106 (6)	-0.0090 (6)	-0.0235 (6)
F3	0.0997 (10)	0.0570 (8)	0.0663 (8)	-0.0309 (7)	-0.0009 (7)	0.0030 (6)
N1	0.0434 (12)	0.0312 (10)	0.0307 (10)	0.000	0.0065 (9)	0.000
N2	0.0413 (8)	0.0373 (8)	0.0316 (8)	0.0031 (7)	0.0036 (6)	-0.0016 (6)
C2	0.0476 (10)	0.0339 (10)	0.0336 (9)	0.0044 (8)	0.0077 (8)	0.0027 (7)
C3	0.0710 (14)	0.0346 (10)	0.0429 (11)	0.0078 (10)	0.0041 (10)	0.0056 (8)
C4	0.088 (2)	0.0300 (14)	0.0558 (18)	0.000	0.0083 (16)	0.000
C5	0.0465 (10)	0.0387 (10)	0.0320 (9)	0.0088 (8)	0.0013 (8)	0.0018 (8)
C6	0.0361 (10)	0.0380 (9)	0.0360 (9)	0.0060 (8)	0.0004 (8)	-0.0033 (8)
C7	0.0464 (11)	0.0434 (11)	0.0372 (10)	0.0040 (8)	0.0051 (8)	-0.0018 (8)
C8	0.0555 (12)	0.0616 (13)	0.0332 (10)	0.0073 (10)	-0.0002 (9)	-0.0080 (9)
C9	0.0424 (11)	0.0463 (12)	0.0501 (11)	0.0038 (9)	-0.0017 (9)	-0.0147 (9)
C10	0.0491 (11)	0.0427 (11)	0.0499 (12)	-0.0027 (9)	0.0022 (9)	-0.0009 (9)
C11	0.0517 (11)	0.0448 (11)	0.0372 (10)	0.0001 (9)	-0.0018 (8)	0.0006 (8)

Geometric parameters (\AA , $^\circ$)

Ni1—N1	1.9508 (19)	C3—C4	1.382 (2)
Ni1—N2 ⁱ	2.1878 (13)	C3—H3	0.9300
Ni1—N2	2.1878 (13)	C4—C3 ⁱ	1.382 (2)
Ni1—Cl1 ⁱ	2.2464 (5)	C4—H4	0.9300
Ni1—Cl1	2.2464 (5)	C5—H5	0.9300
F1—C7	1.347 (2)	C6—C7	1.379 (2)
F2—C9	1.3400 (19)	C6—C11	1.393 (3)
F3—C10	1.347 (2)	C7—C8	1.374 (3)
N1—C2 ⁱ	1.3354 (18)	C8—C9	1.370 (3)
N1—C2	1.3354 (18)	C8—H8	0.9300
N2—C5	1.277 (2)	C9—C10	1.368 (3)
N2—C6	1.424 (2)	C10—C11	1.367 (3)
C2—C3	1.384 (3)	C11—H11	0.9300
C2—C5	1.462 (2)		
N1—Ni1—N2 ⁱ	77.32 (4)	C3—C4—H4	120.1
N1—Ni1—N2	77.32 (4)	C3 ⁱ —C4—H4	120.1
N2 ⁱ —Ni1—N2	154.64 (8)	N2—C5—C2	117.50 (15)
N1—Ni1—Cl1 ⁱ	113.393 (16)	N2—C5—H5	121.2
N2 ⁱ —Ni1—Cl1 ⁱ	91.20 (4)	C2—C5—H5	121.2
N2—Ni1—Cl1 ⁱ	98.82 (4)	C7—C6—C11	117.64 (16)
N1—Ni1—Cl1	113.393 (16)	C7—C6—N2	125.03 (17)
N2 ⁱ —Ni1—Cl1	98.82 (4)	C11—C6—N2	117.31 (16)
N2—Ni1—Cl1	91.20 (4)	F1—C7—C8	117.93 (17)
Cl1 ⁱ —Ni1—Cl1	133.21 (3)	F1—C7—C6	119.18 (16)

C2 ⁱ —N1—C2	121.0 (2)	C8—C7—C6	122.88 (18)
C2 ⁱ —N1—Ni1	119.52 (10)	C9—C8—C7	118.05 (18)
C2—N1—Ni1	119.52 (10)	C9—C8—H8	121.0
C5—N2—C6	122.00 (15)	C7—C8—H8	121.0
C5—N2—Ni1	111.45 (11)	F2—C9—C10	119.38 (18)
C6—N2—Ni1	126.33 (11)	F2—C9—C8	120.18 (18)
N1—C2—C3	120.88 (17)	C10—C9—C8	120.44 (17)
N1—C2—C5	113.77 (15)	F3—C10—C11	120.20 (17)
C3—C2—C5	125.34 (16)	F3—C10—C9	118.48 (16)
C4—C3—C2	118.68 (18)	C11—C10—C9	121.32 (18)
C4—C3—H3	120.7	C10—C11—C6	119.65 (17)
C2—C3—H3	120.7	C10—C11—H11	120.2
C3—C4—C3 ⁱ	119.8 (3)	C6—C11—H11	120.2
N2 ⁱ —Ni1—N1—C2 ⁱ	4.58 (9)	Ni1—N2—C5—C2	6.53 (19)
N2—Ni1—N1—C2 ⁱ	-175.42 (9)	N1—C2—C5—N2	-3.1 (2)
Cl1 ⁱ —Ni1—N1—C2 ⁱ	-81.18 (9)	C3—C2—C5—N2	175.64 (17)
Cl1—Ni1—N1—C2 ⁱ	98.82 (9)	C5—N2—C6—C7	-33.8 (3)
N2 ⁱ —Ni1—N1—C2	-175.42 (9)	Ni1—N2—C6—C7	140.38 (15)
N2—Ni1—N1—C2	4.58 (9)	C5—N2—C6—C11	147.89 (17)
Cl1 ⁱ —Ni1—N1—C2	98.82 (9)	Ni1—N2—C6—C11	-37.9 (2)
Cl1—Ni1—N1—C2	-81.18 (9)	C11—C6—C7—F1	178.61 (16)
N1—Ni1—N2—C5	-6.01 (11)	N2—C6—C7—F1	0.3 (3)
N2 ⁱ —Ni1—N2—C5	-6.01 (11)	C11—C6—C7—C8	-0.1 (3)
Cl1 ⁱ —Ni1—N2—C5	-118.15 (11)	N2—C6—C7—C8	-178.39 (17)
Cl1—Ni1—N2—C5	107.72 (12)	F1—C7—C8—C9	-179.78 (17)
N1—Ni1—N2—C6	179.28 (14)	C6—C7—C8—C9	-1.1 (3)
N2 ⁱ —Ni1—N2—C6	179.28 (14)	C7—C8—C9—F2	-178.30 (16)
Cl1 ⁱ —Ni1—N2—C6	67.14 (13)	C7—C8—C9—C10	1.0 (3)
Cl1—Ni1—N2—C6	-66.99 (13)	F2—C9—C10—F3	-0.2 (3)
C2 ⁱ —N1—C2—C3	-1.51 (13)	C8—C9—C10—F3	-179.49 (18)
Ni1—N1—C2—C3	178.49 (13)	F2—C9—C10—C11	179.53 (17)
C2 ⁱ —N1—C2—C5	177.34 (16)	C8—C9—C10—C11	0.2 (3)
Ni1—N1—C2—C5	-2.66 (16)	F3—C10—C11—C6	178.29 (17)
N1—C2—C3—C4	3.0 (2)	C9—C10—C11—C6	-1.4 (3)
C5—C2—C3—C4	-175.74 (15)	C7—C6—C11—C10	1.3 (3)
C2—C3—C4—C3 ⁱ	-1.44 (12)	N2—C6—C11—C10	179.76 (16)
C6—N2—C5—C2	-178.49 (15)		

Symmetry code: (i) $-x+1, y, -z+1/2$.