# metal-organic compounds

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

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The asymmetric unit of the title compound, [NiCl$_2$(C$_{19}$H$_9$F$_6$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$_2$N$_3$ geometry, with two Cl atoms in the equatorial plane. In the crystal, molecules are linked by intermolecular C—F···$\pi$ [F···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).
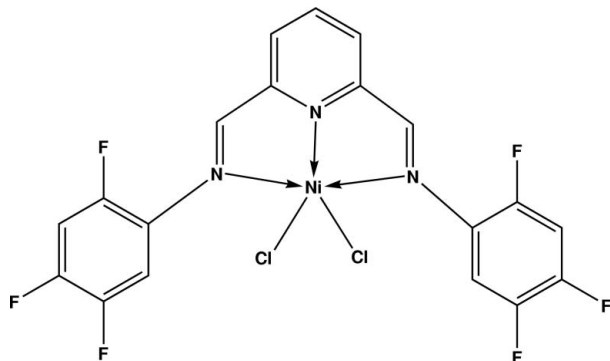


## Experimental

### Crystal data

| | |
|---|---|
| [NiCl$_2$(C$_{19}$H$_9$F$_6$N$_3$)] | $V = 1919.4$ (2) Å$^3$ |
| $M_r = 522.90$ | $Z = 4$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation |
| $a = 18.0947$ (13) Å | $\mu = 1.36$ mm$^{-1}$ |
| $b = 8.8967$ (6) Å | $T = 298$ K |
| $c = 12.1638$ (9) Å | $0.32 \times 0.16 \times 0.06$ mm |
| $\beta = 101.421$ (2)° | |

### Data collection

| | |
|---|---|
| Bruker SMART APEX CCD area-detector diffractometer | 7821 measured reflections |
| | 1751 independent reflections |
| Absorption correction: analytical (*SHELXTL*; Sheldrick, 2008) | 1482 reflections with $I > 2\sigma(I)$ |
| $T_{min} = 0.740$, $T_{max} = 0.921$ | $R_{int} = 0.033$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.025$ | 142 parameters |
| $wR(F^2) = 0.058$ | H-atom parameters constrained |
| $S = 0.96$ | $\Delta\rho_{max} = 0.23$ e Å$^{-3}$ |
| 1751 reflections | $\Delta\rho_{min} = -0.20$ 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*.

## 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.
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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.
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**supplementary materials**

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

## O. Baldovino-Pantaleón, S. Hernández-Ortega, R. Reyes-Martínez and D. Morales-Morales

### 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 2$_1$/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 clasic aceptor-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).

### Experimental

A solution of the ligand {C$_5$H$_3$N-2,6-(CH=N—C$_6$H$_2$-2,4,5-F$_3$)$_2$} (120 mg, 0.33 mmol) in anhydrous CH$_2$Cl$_2$ (10 ml) was added to a stirred solution of NiCl$_2$.6 H$_2$O(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

### Refinement

H atoms were included in calculated positions (C—H = 0.93 Å), and refined using a riding model,with $U_{iso}$(H) = 1.2$U_{eq}$ of the carrier atom.
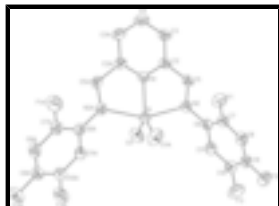
# supplementary materials

**Figures**



Fig. 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- $\kappa^3 N,N',N''$}dichloridonickel(II)

*Crystal data*

| | |
|---|---|
| [NiCl$_2$(C$_{19}$H$_9$F$_6$N$_3$)] | $F(000) = 1040$ |
| $M_r = 522.90$ | $D_x = 1.810$ Mg m$^{-3}$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -C 2yc | Cell parameters from 5009 reflections |
| $a = 18.0947$ (13) Å | $\theta = 2.6–32.1°$ |
| $b = 8.8967$ (6) Å | $\mu = 1.36$ mm$^{-1}$ |
| $c = 12.1638$ (9) Å | $T = 298$ K |
| $\beta = 101.421$ (2)° | Prism, red |
| $V = 1919.4$ (2) Å$^3$ | $0.32 \times 0.16 \times 0.06$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART APEX CCD area-detector diffractometer | 1751 independent reflections |
| Radiation source: fine-focus sealed tube | 1482 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.033$ |
| Detector resolution: 0.83 pixels mm$^{-1}$ | $\theta_{max} = 25.3°$, $\theta_{min} = 2.3°$ |
| $\omega$ scans | $h = -21 \rightarrow 21$ |
| Absorption correction: analytical (*SHELXTL*; Sheldrick, 2008) | $k = -10 \rightarrow 10$ |
| $T_{min} = 0.740$, $T_{max} = 0.921$ | $l = -14 \rightarrow 14$ |
| 7821 measured reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.025$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.058$ | H-atom parameters constrained |
| $S = 0.96$ | $w = 1/[\sigma^2(F_o^2) + (0.034P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |

| | |
|---|---|
| 1751 reflections | $(\Delta/\sigma)_{max} < 0.001$ |
| 142 parameters | $\Delta\rho_{max} = 0.23$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -0.20$ e Å$^{-3}$ |

*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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| 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 (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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 (Å, °)*

| | | | |
|---|---|---|---|
| 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 codes: (i) −$x$+1, $y$, −$z$+1/2.

### Table 1

*Table 1. Intermolecular and intramolecular interaction C-F–π, C-H–π, π–π of (I) (Å)*

| H/F/centroid | centroid/F | distance | Symmetry-code |
|---|---|---|---|
| H8 | F3 | 2.652 | (i) |
| H8 | F2 | 2.648 | (ii) |
| F1 | F2 | 2.903 | (iii) |
| F1 | N1-C4 | 2.968 | (iv) |

(i) x, 2-y, 1.5 +z; (ii) -x+1.5, +y-1/2', -z+1.5; (iii) -x+1.5, 1.5+y, -z+1.5; (iv) x, -y+1, z-1/2

**Fig. 1**