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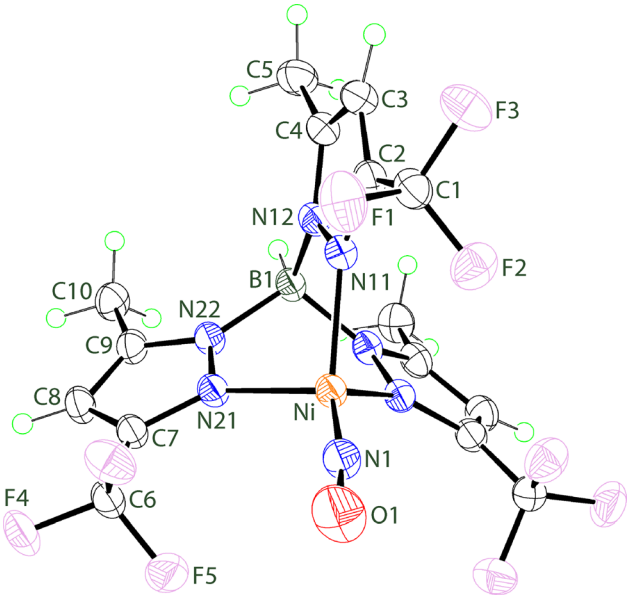
# The crystal structure of nitroxyl-κ*N*-{hydridotris(3-trifluoromethyl-5-methylpyrazolyl-1-yl-κ$N^3$)borato}nickel(II), $C_{15}H_{13}BF_9N_7NiO$

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**Abstract**

$C_{15}H_{13}BF_9N_7NiO$, orthorhombic, *Pnma* (no. 62), $a = 17.8513(3)$ Å, $b = 13.3869(2)$ Å, $c = 8.5944(2)$ Å, $V = 2053.83(7)$ Å$^3$, $Z = 4$, $R_{gt}(F) = 0.0235$, $wR_{ref}(F^2) = 0.0690$, $T = 124(2)$ K.

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**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Blue block |
| Size: | 0.10 × 0.05 × 0.04 mm |
| Wavelength: | Mo *K*α radiation (0.71073 Å) |
| $\mu$: | 1.05 mm$^{-1}$ |
| Diffractometer, scan mode: | Rigaku XtaLAB P200, $\omega$ |
| $\theta_{max}$, completeness: | 27.5°, >99% |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 32,121, 2455, 0.019 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\sigma(I_{obs})$, 2314 |
| $N(param)_{refined}$: | 173 |
| Programs: | CrysAlis$^{PRO}$ [1], SIR2014 [2], SHELX [3], WinGX/ORTEP [4] |

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

## Source of material

The title complex (I) was obtained by modified synthetic procedures from the reaction of $[Ni(NO)(Br)(PPh_3)_2]$ [5, 6] or $[Ni(NO)(I)]_n$ [7] with hydridotris(3-trifluoromethyl-5-methylpyrazolyl-1-yl)borate, $LoF^-$. To a solution of $[Ni(NO)(Br)(PPh_3)_2]$ (0.139 g, 0.201 mmol) in dichloromethane (10 mL) was added K[LoF] (0.0996 g, 0.200 mmol) in dichloromethane (10 mL). The resulting dark-blue solution was stirred under an argon atmosphere for 3 h, after which the solution was filtered through Celite to remove any undissolved powder. To the filtrate, was added one volume equivalent of *n*-heptane. Recrystallisation from this mixture, held at −30 °C, gave dark-blue crystals. Yield: 0.0437 g, 0.0798 mmol (40%).

The second method had $[Ni(NO)(I)]_n$ as the nickel source. Thus, $[Ni(NO)(I)]_n$ (0.164 g, 0.761 mmol) was reacted with K[Lof] (0.332 g, 0.666 mmol) in acetone (10 mL). The resulting dark-blue solution was stirred under an argon atmosphere for 1 h. The solution was filtered off through Celite to remove any undissolved powder. The filtrate was evaporated under vacuum. The resulting solid was recrystallised from ethanol/tetrahydrofuran (1:1) at −30 °C to give dark-blue crystals. Yield: 0.178 g,

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**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$).

| Atom | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Ni | 0.33867 (2) | 0.250000 | 0.39357 (3) | 0.02390 (9) |
| F1 | 0.40975 (5) | −0.01000 (8) | 0.28207 (11) | 0.0473 (2) |
| F2 | 0.42568 (5) | 0.11657 (7) | 0.13338 (11) | 0.0415 (2) |
| F3 | 0.38823 (5) | −0.02285 (7) | 0.03699 (11) | 0.0448 (2) |
| F4 | 0.30823 (8) | 0.250000 | 0.95749 (13) | 0.0417 (3) |
| F5 | 0.36748 (5) | 0.17008 (7) | 0.77790 (10) | 0.0420 (2) |
| O1 | 0.48522 (9) | 0.250000 | 0.5066 (2) | 0.0564 (5) |
| N1 | 0.42622 (9) | 0.250000 | 0.44993 (19) | 0.0312 (3) |
| N11 | 0.28345 (6) | 0.14722 (8) | 0.26697 (12) | 0.0255 (2) |
| N12 | 0.20739 (6) | 0.15594 (8) | 0.25877 (12) | 0.0262 (2) |
| N21 | 0.25714 (8) | 0.250000 | 0.55595 (17) | 0.0251 (3) |
| N22 | 0.18437 (9) | 0.250000 | 0.50719 (18) | 0.0254 (3) |
| C1 | 0.38091 (8) | 0.03826 (10) | 0.15925 (16) | 0.0316 (3) |
| C2 | 0.30112 (7) | 0.06736 (10) | 0.18165 (14) | 0.0279 (3) |
| C3 | 0.23745 (8) | 0.02247 (11) | 0.11978 (16) | 0.0323 (3) |
| H3 | 0.235032 | −0.035242 | 0.055644 | 0.039* |
| C4 | 0.17856 (8) | 0.08026 (10) | 0.17211 (15) | 0.0299 (3) |
| C5 | 0.09637 (8) | 0.06648 (12) | 0.14620 (18) | 0.0379 (3) |
| H5A | 0.069968 | 0.071360 | 0.245889 | 0.057* |
| H5B | 0.087290 | 0.000605 | 0.100177 | 0.057* |
| H5C | 0.077977 | 0.118446 | 0.075546 | 0.057* |
| C6 | 0.32425 (11) | 0.250000 | 0.8056 (2) | 0.0305 (4) |
| C7 | 0.25410 (11) | 0.250000 | 0.7116 (2) | 0.0270 (4) |
| C8 | 0.18067 (11) | 0.250000 | 0.7639 (2) | 0.0306 (4) |
| H8 | 0.163846 | 0.250000 | 0.868784 | 0.037* |
| C9 | 0.13699 (11) | 0.250000 | 0.6304 (2) | 0.0287 (4) |
| C10 | 0.05361 (11) | 0.250000 | 0.6139 (2) | 0.0347 (4) |
| H10A | 0.030469 | 0.250000 | 0.717268 | 0.052* |
| H10B[a] | 0.037857 | 0.309772 | 0.556740 | 0.052* |
| H10C[a] | 0.037857 | 0.190228 | 0.556740 | 0.052* |
| B1 | 0.16920 (11) | 0.250000 | 0.3297 (2) | 0.0262 (4) |
| H1 | 0.107581 | 0.249999 | 0.305203 | 0.031* |

[a]Occupancy: 0.5.

0.325 mmol (49%). **$^1$H NMR** ($CDCl_3$, 500 MHz): $\delta$ 2.26 (s, 9H, $CH_3$), 6.47 (s, 3H, pz-4H). **$^{13}$C{$^1$H} NMR** ($CDCl_3$, 125 MHz): $\delta$ 12.4 ($CH_3$), 106.0 (pz-4C), 122.5 ($CF_3$, q, $J_{C,F}$ = 269 Hz), 145.0 (pz-3C, q, $J_{C,F}$ = 38 Hz), 145.9 (pz-5C). **Anal. Calcd.** for $C_{15}H_{13}BF_9N_7NiO$. C, 32.89; H, 2.39; N, 17.90%. Found: C, 32.69; H, 2.35, N, 17.99%. **IR** (KBr, cm$^{-1}$) 2564 m ($\nu$B–H), 1823 versus ($\nu$N–O). **UV–Vis** ($CH_2Cl_2$, $\lambda_{max}$/nm) ($\varepsilon$ M$^{-1}$ cm$^{-1}$): 593 (440), 249 (13,000). The spectral details recorded for (I) obtained from the $[Ni(NO)(Br)(PPh_3)_2]$ precursor were identical.

## Experimental details

The B- and C-bound H atoms were geometrically placed (B–H = 1.12 Å and C–H = 0.98 Å) and refined as riding with $U_{iso}$(H) = 1.2$U_{eq}$(B) and $U_{iso}$(H) = 1.5$U_{eq}$(C), respectively. Owing to poor agreement, one reflection affected by the beam-stop, i.e. (2 0 0), was removed from the final cycles of refinement.

## Comment

Nitric oxide (NO) is a non-innocent ligand [8] which readily coordinates many transition metal ions, often to form stable NO-containing complexes [9]. Previous interest in transition metal NO complexes led to experiments with the anionic, sterically hindered $N_3$-tripodal ligand, hydridotris[3-(*t*-butyl)-5-isopropylpyrazol-1-yl]borate, hereafter denoted as $L^-$, where certain control over the coordination sphere can be exerted by the relatively large *t*-butyl substituent [10]. In continuation of this interest, a series complexes, namely Fe(L)($^3NO^-$), Co(L)($^3NO^-$), Ni(L)($^3NO^-$) and Cu(L)($NO^{\cdot}$) [10]; in the Cu complex the NO ligand is present as a radical, i.e. $NO^{\cdot}$, while the other NO ligands are functioning as a nitroxyl anion, i.e. ($^3NO^-$) [10]. Their electronic structures were investigated by DFT calculations and some physicochemical properties determined [10]. A particular interest was to determine how the electronic states of the supporting ligands can affect the properties and reactivity of the complexes. This research led to the synthesis of title nickel(II) complex, Ni(Lof)NO, (I), where the tripodal ligand, $LoF^-$, is the hydridotris(3-trifluoromethyl-5-methylpyrazolyl-1-yl)borate anion which features an electron-withdrawing $CF_3$ substituent. The $CF_3$ group has unique electronegativity, hydrophobicity, metabolic stability and bioavailability, and is widely found in organic molecules [11, 12]. Complex (I) was obtained by the reaction of $[Ni(NO)(Br)(PPh_3)_2Br]$ or $[Ni(NO)(I)]_n$ with K[LoF].

The molecular structure of (I) is shown in the figure (50% displacement ellipsoids). The crystallographic asymmetric-unit comprises half a molecule as the complex is bisected by a mirror plane. The Ni atom is coordinated by the three N atoms of the tripodal ligand and the NO–N atom. The Ni–N11 and Ni–N21 bond lengths [2.0121(11) and 2.0164(15) Å] are experimentally equivalent and considerably longer than the Ni–N1 [1.6361(16) Å] bond; the N1–O1 bond length is 1.160(2) Å. The presence of the tripodal ligand, with a restricted bite distance, introduces significant distortions in the $N_4$-coordination geometry. Thus the range of N–Ni–N angles is substantial with the narrowest angle being 86.28(6)°, for N11–Ni–N11$^i$, and the widest being 128.90(4)°, for N1–Ni–N11; symmetry operation (i): $x$, $1/2-y$, $z$. The value of $\tau_4 = [360 - (\alpha + \beta)/141] = 0.73$, where $\alpha$ and $\beta$ are the two widest angles subtended at the metal centre [13]. The value compares with 0.00 for an ideal square-planar geometry, 0.85 for a trigonal-pyramidal

arrangement and 1.00 for a tetrahedral geometry. Indeed, the value of $\tau_4$ in (I) is closest to 0.64 which corresponds to a see-saw geometry. The Ni–N1–O1 angle is 172.42(17)°. When viewed down the B1–Ni axis, the molecule approximates three-fold symmetry.

There are two closely related nickel(II) complexes available for comparison, namely the dimethyl $L^-$ derivative [6] and the mixed *i*-Pr and *t*-Bu $L^-$ species [5], hereafter (II) and (III), respectively. Two independent half-molecules comprise the asymmetric unit in (II), each disposed about a mirror plane. In (III), where the *t*-Bu groups are proximate to the nickel atom, the complex also has crystallographically imposed mirror symmetry. The values of $\tau_4$ for (II) are 0.76 and 0.75, and for (III), 0.79, both indicative of distortions towards a trigonal-pyramidal geometry. The respective ranges of Ni–N(tripodal) bond lengths for (I)–(III) are 2.0121(11)–2.0164(15) Å, 1.980(3)–2.006(4) Å, and 2.026(3)–2.024(5) Å, suggesting a trend in bond lengths (II) < (I) < (III) which correlates with the steric bulk of the substituent proximate to the nickel(II) centre, i.e. Me < $CF_3$ < *t*-Bu. The Ni–N(NO) bond lengths are 1.6361(16) Å, 1.619(6) & 1.617(6) Å and 1.651(6) Å for (I)–(III), respectively, again, consistent with steric hindrance at the metal centre.

The strong $\nu$(N–O) band observed in the IR spectra is very sensitive to nature of the tripodal ligands. Thus, the $\nu$(N–O) band (I) was measured at 1823 $cm^{-1}$, which compares to 1786 $cm^{-1}$ in (II) and 1780 $cm^{-1}$ in (III). These variations might correlate with the Ni–N–O bond angles which follow the order 172.45(17)°, 175.3(7) & 178.5(6)° and 179.1(7)° for (I)–(III), respectively. Hence, the $CF_3$ substituent leads to lower $\nu$(N–O) by ca 40 $cm^{-1}$, due to the change in Ni–NO $\pi$ bonding interaction [5, 9, 10]. Similar trends are observed in $\nu$(C–O) frequencies observed in a series of copper(I) carbonyl complexes ligated by the hydridotris(pyrazolyl)borate ligands [12, 14].

As indicated above, the oxidation state of the nickel atoms in all three complex is +II, and the metal centre is in the high-spin state. Therefore, the total spin of the Ni(II) centre should be $S$ = 1. However, the NMR spectra clearly indicate that (I) is diamagnetic ($S$ = 0). This originates from antiferromagnetic coupling between the d-electrons of the Ni(II) centre ($S_{tot}$ = 1) and the $\pi^*$-electrons of the nitroxyl anion ($^3NO^-$) ($S$ = 1), so that, $S$ = 1, consistent with diamagnetic behaviour [5, 10, 15].

The molecular packing of (I) was analysed employing PLATON [16]. The NO–O1 atom participates in two independent C–H···O interactions, both with a methyl-bound H atom derived from two different methyl groups [C5–H5c···O1$^{ii}$: H5c···O1$^{ii}$ = 2.52 Å, C5···O1$^{ii}$ = 3.4201(19) Å with angle at H5c = 153° for (ii): –1/2 + $x$, 1/2 – $y$, 1/2 – $z$; C10–H10c···O1$^{iii}$: H10c···O1$^{iii}$ = 2.52 Å, C10···O1$^{iii}$ = 3.483(2) Å with angle at H10c = 174° for (iii): –1/2 + $x$, 1/2 – $y$, 3/2 – $z$]. With the application of mirror symmetry, these interactions extend in two-dimensions and lead to supramolecular layers in the *ab*-plane which stack along the *c*-axis. From a consideration of close interatomic separations, the most directional interactions between layers to give rise to a three-dimensional architecture are C–F···$\pi$(pyrazoyl) interactions [C6–F4···Cg(N11, N12, C2–C4)$^{iv}$: F4···Cg(N11, N12, C2–C4)$^{iv}$ = 3.1748(11) Å with angle at F4 = 136.15(4) Å for (iv): $x$, $y$, 1 + $z$].

Using standard methods [17], a surface contact analysis of the molecular packing was conducted employing CrystalExplorer [18]. This analysis points to the obvious prominence of H and F in surface contacts. This is reflected in the large percentage of F···H/H···F [49.5%] contacts. H participates in 30.4% of all other contacts, viz. O···H/H···O [10.4%], N···H/H···N [7.9%], C···H/H···C [5.9%], H···H [6.0%] and Ni···H/H···Ni [0.2%] while F participates in 19.5% of the remaining contacts which include F···C/C···F [8.7%], F···F [6.9%] and F···N/N···F [3.9%]. The remaining percentage surface contacts are due to C···C [0.6%].

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