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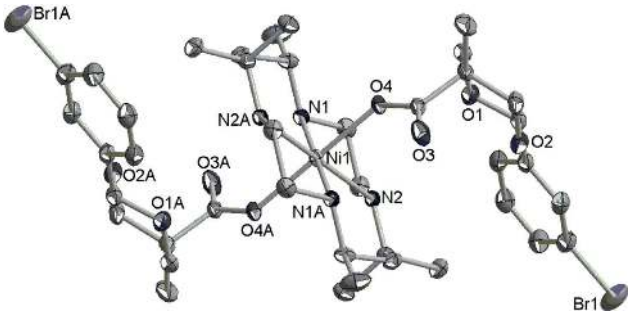
# Crystal structure of bis[(2-(3-bromophenyl)-5-methyl-1,3-dioxane-5-carboxylato-$\kappa$-*O*)-(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-$\kappa^4$*N*,*N*′,*N*″,*N*‴)]nickel(II), $C_{40}H_{60}Br_2N_4NiO_8$

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## Abstract

$C_{40}H_{60}Br_2N_4NiO_8$, triclinic, $P\bar{1}$ (no. 2), $a = 8.546(7)$ Å, $b = 10.162(7)$ Å, $c = 13.831(13)$ Å, $\alpha = 92.943(9)°$, $\beta = 101.096(8)°$, $\gamma = 111.710(5)°$, $V = 1085.1(15)$ Å$^3$, $Z = 1$, $R_{gt}(F) = 0.0317$, $wR_{ref}(F^2) = 0.0905$, $T = 296(2)$ K.

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The crystal 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

An acetonitrile solution (20 mL) of $[NiL](ClO_4)_2$(0.270 g, 0.5 mmol) (L = *trans*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) was added to a solution of (2-(3-bromophenyl)-5-methyl-1,3-dioxane-5-carboxylic acid (0.301 g, 1.0 mmol) and NaOH (0.04 g, 1.0 mmol) in the minimum amount of water. Crystals of the title compound were obtained by slow evaporation within 5 days.

## Experimental details

The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined

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

| | |
|---|---|
| Crystal: | Blue block |
| Size: | 0.45 × 0.36 × 0.32 mm |
| Wavelength: | Mo $K\alpha$ radiation (0.71073 Å) |
| $\mu$: | 2.34 mm$^{-1}$ |
| Diffractometer, scan mode: | Bruker APEX-II, $\varphi$ and $\omega$-scans |
| $\theta_{max}$, completeness: | 27.5°, >97% |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 12205, 4787, 0.023 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 3927 |
| $N(param)_{refined}$: | 254 |
| Programs: | Bruker programs [1], SHELX [2, 3], DIAMOND [4] |

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

| Atom | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br1 | −0.21714(4) | 0.51494(3) | −0.06595(3) | 0.08254(13) |
| Ni1 | 0.5000 | 1.0000 | 0.5000 | 0.02777(9) |
| O1 | 0.2720(2) | 1.11420(16) | 0.20751(11) | 0.0475(4) |
| O2 | 0.35553(19) | 0.96579(16) | 0.11439(11) | 0.0468(3) |
| O3 | 0.7057(2) | 1.0292(2) | 0.30164(12) | 0.0586(4) |
| O4 | 0.55834(17) | 1.12103(14) | 0.38126(9) | 0.0370(3) |
| N1 | 0.3543(2) | 1.11582(16) | 0.52845(12) | 0.0325(3) |
| H1A | 0.3087 | 1.0815 | 0.5863 | 0.039* |
| N2 | 0.27779(19) | 0.86966(16) | 0.39373(11) | 0.0312(3) |
| H2A | 0.2954 | 0.9092 | 0.3317 | 0.037* |
| C1 | −0.1526(3) | 0.6824(3) | 0.02499(17) | 0.0514(5) |
| C2 | −0.2706(3) | 0.6935(3) | 0.07717(19) | 0.0553(6) |
| H29 | −0.3784 | 0.6196 | 0.0691 | 0.066* |
| C3 | −0.2248(3) | 0.8165(3) | 0.14139(18) | 0.0551(6) |
| H1 | −0.3033 | 0.8267 | 0.1763 | 0.066* |
| C4 | −0.0633(3) | 0.9250(3) | 0.15447(16) | 0.0501(5) |
| H2 | −0.0340 | 1.0076 | 0.1980 | 0.060* |
| C5 | 0.0556(3) | 0.9114(2) | 0.10290(15) | 0.0426(5) |
| C6 | 0.2325(3) | 1.0277(2) | 0.11624(15) | 0.0449(5) |
| H27 | 0.2324 | 1.0860 | 0.0620 | 0.054* |
| C7 | 0.4364(3) | 1.2304(2) | 0.22158(17) | 0.0508(5) |
| H26 | 0.4624 | 1.2868 | 0.2856 | 0.061* |
| H3 | 0.4311 | 1.2916 | 0.1705 | 0.061* |
| C8 | 0.5801(3) | 1.1777(2) | 0.21700(15) | 0.0440(5) |
| C9 | 0.5239(3) | 1.0748(3) | 0.12136(15) | 0.0515(6) |
| H5 | 0.5213 | 1.1270 | 0.0647 | 0.062* |
| H4 | 0.6068 | 1.0308 | 0.1200 | 0.062* |
| C10 | 0.6176(2) | 1.1013(2) | 0.30713(14) | 0.0363(4) |
| C11 | 0.2045(2) | 1.0693(2) | 0.44294(15) | 0.0388(4) |
| H25 | 0.2387 | 1.1147 | 0.3862 | 0.047* |
| H7 | 0.1142 | 1.0964 | 0.4592 | 0.047* |

**Table 2** (continued)

| Atom | x | y | z | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C12 | 0.1380(2) | 0.9081(2) | 0.41807(16) | 0.0394(4) |
| H8 | 0.1014 | 0.8627 | 0.4744 | 0.047* |
| H9 | 0.0392 | 0.8752 | 0.3619 | 0.047* |
| C13 | 0.2351(3) | 0.7130(2) | 0.36800(15) | 0.0369(4) |
| C14 | 0.5985(3) | 1.3052(2) | 0.64393(16) | 0.0415(5) |
| H11 | 0.5540 | 1.2456 | 0.6929 | 0.050* |
| H10 | 0.6313 | 1.4036 | 0.6723 | 0.050* |
| C15 | 0.4490(3) | 1.2724(2) | 0.55401(16) | 0.0403(4) |
| H16 | 0.4971 | 1.3095 | 0.4975 | 0.048* |
| C16 | 0.3318(3) | 1.3485(3) | 0.5744(3) | 0.0681(8) |
| H12 | 0.2363 | 1.3253 | 0.5182 | 0.102* |
| H13 | 0.3966 | 1.4499 | 0.5858 | 0.102* |
| H14 | 0.2890 | 1.3180 | 0.6322 | 0.102* |
| C17 | 0.1600(3) | 0.6286(2) | 0.44740(17) | 0.0474(5) |
| H17 | 0.2333 | 0.6728 | 0.5117 | 0.071* |
| H18 | 0.1529 | 0.5324 | 0.4356 | 0.071* |
| H19 | 0.0465 | 0.6274 | 0.4450 | 0.071* |
| C18 | 0.1050(3) | 0.6570(2) | 0.26785(17) | 0.0522(6) |
| H21 | 0.1530 | 0.7090 | 0.2174 | 0.078* |
| H20 | 0.0004 | 0.6694 | 0.2721 | 0.078* |
| H22 | 0.0798 | 0.5573 | 0.2511 | 0.078* |
| C19 | 0.0092(3) | 0.7884(3) | 0.03642(16) | 0.0472(5) |
| H28 | 0.0863 | 0.7780 | 0.0004 | 0.057* |
| C20 | 0.7490(4) | 1.3040(3) | 0.2165(2) | 0.0710(8) |
| H32 | 0.7829 | 1.3697 | 0.2764 | 0.107* |
| H30 | 0.7311 | 1.3520 | 0.1599 | 0.107* |
| H31 | 0.8382 | 1.2692 | 0.2130 | 0.107* |

first isotropically and then anisotropically. All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. The $U_{iso}$ values of the hydrogen atoms of methyl groups were set to $1.5U_{eq}$(C) and the $U_{iso}$ values of all other hydrogen atoms were set to $1.2U_{eq}$(C, N).

## Discussion

Some metal compounds have attracted much attention owing to their widely application in fragrance and flavors and a protection of carbonyl or synthetic intermediate [5]. The title compound was synthesized by the reaction of (2-(3-bromophenyl)-5-methyl-1,3-dioxane-5-carboxylic acid with $[NiL](ClO_4)_2$. X-ray crystal structural analysis reveals that the asymmetric unit of the title structure contains one half of a cation $[NiL]^{2+}$, and one anion $[C_{12}H_{12}O_4Br]^-$. The central Ni(II) atom displays a six-coordinate octahedral coordination geometry by coordination with four nitrogen atoms from L, and two oxygen atoms from (2-(3-bromophenyl)-5-methyl-1,3-dioxane-5-carboxylate. The Ni-N bond lengths [2.0777(18)–2.0942(19) Å] are slightly shorter than the Ni—O bond lengths [2.1277(18) Å]. The anion $[ClO_4]^-$, different from the similar structures [6, 7], has not been found in this title structure because the [Ni(*trans*-L)]$^{2+}$ instead of [Ni(rac-L)]$^{2+}$ was used to form this complex with two anionic and one neutral tetraaza ligand coordinated at Ni(II).

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