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Crystal structure of bis[(2-(2-bromophenyl)-5-ethyl-1,3-dioxane-5-carboxylato- κO)-(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane- $\kappa^4 N, N', N'', N'''$)]nickel(II) hemihydrate
 $C_{42}H_{65}Br_2N_4NiO_{8.5}$

Table 1: Data collection and handling.

Crystal:	Blue block
Size:	$0.45 \times 0.35 \times 0.32$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	2.24 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
θ_{max} , completeness:	27.4° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	24987, 5076, 0.026
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3882
$N(\text{param})_{\text{refined}}$:	263
Programs:	Bruker programs [1], SHELX [2, 3], DIAMOND [4], PLATON [5]

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Abstract

$C_{42}H_{65}Br_2N_4NiO_{8.5}$, monoclinic, $P2_1/c$ (no. 14), $a = 14.852(2)$ Å, $b = 12.1965(18)$ Å, $c = 14.166(2)$ Å, $\beta = 117.755(1)^\circ$, $V = 2270.8(6)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0449$, $wR_{\text{ref}}(F^2) = 0.1276$, $T = 296(2)$ 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) ($L = \text{trans-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane}$) was added to a solution of (2-(2-bromophenyl)-5-ethyl-1,3-dioxane-5-carboxylic acid (0.315 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 7 days.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.5000	0.0000	0.0000	0.02973(13)
Br1	0.20931(4)	0.08608(4)	0.43324(3)	0.08629(19)
O1	0.37744(14)	0.02439(14)	0.03662(15)	0.0377(4)
O2	0.34470(19)	−0.13708(18)	0.0879(2)	0.0652(7)
O3	0.15510(15)	0.02363(16)	0.18742(17)	0.0435(5)
O4	0.17245(16)	0.18363(16)	0.10980(17)	0.0483(5)
N1	0.61702(16)	0.00296(18)	0.15847(17)	0.0360(5)
H1A	0.6790	0.0001	0.1503	0.043*
N2	0.49878(16)	−0.16757(17)	0.02131(17)	0.0338(5)
H2A	0.4437	−0.1823	0.0392	0.041*
C1	0.1049(3)	0.1726(3)	0.3279(3)	0.0583(9)
C2	0.1014(2)	0.1895(2)	0.2292(3)	0.0458(7)
C3	0.0257(3)	0.2558(3)	0.1571(3)	0.0637(9)
H3	0.0225	0.2688	0.0909	0.076*
C4	−0.0460(3)	0.3037(4)	0.1809(5)	0.0900(14)
H4	−0.0971	0.3481	0.1314	0.108*
C5	−0.0403(4)	0.2844(5)	0.2788(5)	0.1011(18)
H5	−0.0887	0.3154	0.2949	0.121*
C6	0.0345(4)	0.2209(4)	0.3528(4)	0.0859(14)
H6	0.0382	0.2101	0.4195	0.103*
C7	0.1772(2)	0.1356(2)	0.2024(2)	0.0405(6)
H7	0.2457	0.1456	0.2618	0.049*
C8	0.2321(2)	−0.0318(2)	0.1706(3)	0.0443(7)
H8A	0.2175	−0.1097	0.1618	0.053*
H8B	0.2979	−0.0218	0.2326	0.053*
C9	0.2358(2)	0.0127(2)	0.0723(2)	0.0367(6)
C10	0.2474(2)	0.1367(2)	0.0846(3)	0.0450(7)
H10A	0.3149	0.1542	0.1408	0.054*
H10B	0.2404	0.1685	0.0187	0.054*
C11	0.1362(2)	−0.0198(3)	−0.0276(3)	0.0569(8)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H11A	0.1213	−0.0958	−0.0201	0.068*
H11B	0.0812	0.0242	−0.0290	0.068*
C12	0.1367(3)	−0.0070(4)	−0.1321(3)	0.0688(10)
H12A	0.1577	0.0661	−0.1378	0.103*
H12B	0.0695	−0.0199	−0.1890	0.103*
H12C	0.1831	−0.0588	−0.1366	0.103*
C13	0.3273(2)	−0.0391(2)	0.0656(2)	0.0383(6)
C14	0.6145(2)	−0.1064(2)	0.2027(2)	0.0453(7)
H14A	0.5611	−0.1086	0.2238	0.054*
H14B	0.6789	−0.1209	0.2652	0.054*
C15	0.5948(2)	−0.1922(2)	0.1180(2)	0.0423(6)
H15A	0.6507	−0.1930	0.1005	0.051*
H15B	0.5905	−0.2641	0.1449	0.051*
C16	0.4783(2)	−0.2356(2)	−0.0728(2)	0.0431(6)
H16	0.5313	−0.2206	−0.0938	0.052*
C17	0.4794(3)	−0.3579(3)	−0.0504(3)	0.0668(10)
H17A	0.5437	−0.3774	0.0085	0.100*
H17B	0.4696	−0.3986	−0.1125	0.100*
H17C	0.4257	−0.3748	−0.0330	0.100*
C18	0.3757(2)	−0.2044(2)	−0.1657(2)	0.0469(7)
H18A	0.3274	−0.1989	−0.1377	0.056*
H18B	0.3540	−0.2654	−0.2154	0.056*
C19	0.6350(2)	0.0995(2)	0.2307(2)	0.0433(6)
C20	0.7448(3)	0.0973(3)	0.3228(3)	0.0631(9)
H20A	0.7561	0.0298	0.3615	0.095*
H20B	0.7547	0.1579	0.3699	0.095*
H20C	0.7920	0.1029	0.2943	0.095*
C21	0.5607(3)	0.1001(3)	0.2765(3)	0.0570(8)
H21A	0.4927	0.0904	0.2200	0.086*
H21B	0.5653	0.1689	0.3115	0.086*
H21C	0.5771	0.0415	0.3271	0.086*

Experimental details

The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms. All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters. The *U*_{iso} values of the hydrogen atoms of methyl groups were set to 1.5 *U*_{eq}(C) and the *U*_{iso} values of all other hydrogen atoms were set to 1.2 *U*_{eq}(C, N). We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent water molecules and, thereby, to produce a set of solvent-free diffraction intensities. The SQUEEZE calculations showed a total solvent accessible area volume of 42 Å³ and the residual electron density amounted to 5 e[−] per unit cell, corresponding to half a water molecule per asymmetric unit.

Discussion

Some ketal compounds are of interest because of their widely application in fragrance and flavors and a protection of carbonyl or synthetic intermediate [6]. The title compound was synthesized by the reaction of (2-(2-bromophenyl)-5-ethyl-1,3-dioxane-5-carboxylic acid with [NiL](ClO₄)₂.

X-ray crystal structural analysis reveals that the asymmetric unit of the title structure contains one cation [NiL]²⁺, two anions [C₁₃H₁₄O₄Br][−] and half a water molecule. Different from the similar structures [7, 8], the anion [ClO₄][−] has not been found in this title structure as the charge equilibration if done by another anionic carboxylato ligand. 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-(2-bromophenyl)-5-ethyl-1,3-dioxane-5-carboxylato) ligands. The Ni–N bond lengths [2.067(2)–2.105(2) Å] are slightly shorter than the Ni–O bond length [2.1329(17) Å].

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