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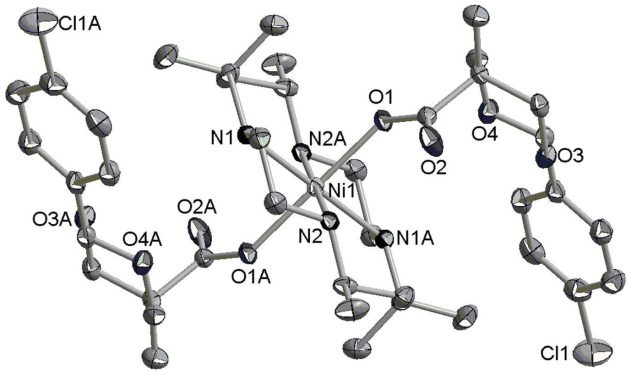
Crystal structure of bis[(2-(4-chlorophenyl)-5-methyl-1,3-dioxane-5-carboxylato-κ^1*O*) (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-κ^4*N*,*N*′,*N*″,*N*‴)]nickel(II), $C_{40}H_{60}Cl_2N_4NiO_8$



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Abstract

$C_{40}H_{60}Cl_2N_4NiO_8$, triclinic, $P\bar{1}$ (no. 2), $a = 8.2372(8)$ Å, $b = 9.7100(10)$ Å, $c = 13.7518(14)$ Å, $\alpha = 100.060(1)°$, $\beta = 101.854(1)°$, $\gamma = 91.675(1)°$, $V = 1057.48(18)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0311$, $wR_{ref}(F^2) = 0.0761$, $T = 296(2)$ K.

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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

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-(4-chlorophenyl)-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 7 days.

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Table 1: Data collection and handling.

Crystal:	Blue block
Size:	0.38 × 0.32 × 0.28 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.64 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	11959, 4718, 0.025
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4049
$N(param)_{refined}$:	254
Programs:	Bruker [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}
Ni1	0.0000	0.0000	0.5000	0.01803(8)
Cl1	−0.80306(6)	−0.43462(6)	0.02763(5)	0.05609(15)
O1	0.02406(13)	0.11517(11)	0.38608(7)	0.0241(2)
O2	0.22135(15)	0.02178(14)	0.31014(9)	0.0361(3)
O3	−0.10606(13)	−0.03727(11)	0.11327(8)	0.0258(2)
O4	−0.25731(14)	0.11289(11)	0.20570(8)	0.0274(2)
N1	0.16418(15)	0.13727(13)	0.61645(9)	0.0210(3)
H1C	0.1589	0.1028	0.6732	0.025*
N2	0.20816(15)	−0.10827(13)	0.48130(9)	0.0207(3)
H2C	0.2430	−0.0808	0.4286	0.025*
C1	0.33026(19)	0.10455(16)	0.59801(12)	0.0247(3)
H1A	0.4149	0.1427	0.6577	0.030*
H1B	0.3513	0.1464	0.5423	0.030*
C2	0.33684(19)	−0.05358(16)	0.57282(12)	0.0242(3)
H2A	0.4457	−0.0770	0.5611	0.029*
H2B	0.3171	−0.0954	0.6288	0.029*
C3	0.17889(19)	−0.26249(16)	0.45591(12)	0.0246(3)
H3	0.1333	−0.2937	0.5095	0.029*
C4	0.3372(2)	−0.33746(18)	0.44763(16)	0.0383(4)
H4A	0.3128	−0.4370	0.4365	0.057*
H4B	0.4192	−0.3088	0.5091	0.057*
H4C	0.3791	−0.3138	0.3920	0.057*
C5	0.0497(2)	−0.30312(17)	0.35628(12)	0.0277(3)
H5A	0.0638	−0.3997	0.3281	0.033*
H5B	0.0775	−0.2462	0.3099	0.033*
C6	0.1355(2)	0.29064(16)	0.64363(12)	0.0252(3)
C7	0.1874(2)	0.37239(17)	0.56875(13)	0.0317(4)
H7A	0.1395	0.3254	0.5010	0.048*
H7B	0.3064	0.3782	0.5786	0.048*
H7C	0.1492	0.4651	0.5794	0.048*
C8	0.2344(2)	0.35100(19)	0.75061(14)	0.0401(4)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H8A	0.3504	0.3383	0.7540	0.060*
H8B	0.1964	0.3033	0.7982	0.060*
H8C	0.2182	0.4492	0.7667	0.060*
C9	0.10054(19)	0.09434(15)	0.31440(11)	0.0220(3)
C10	0.0395(2)	0.17123(16)	0.22514(11)	0.0242(3)
C11	0.1675(2)	0.29214(19)	0.23204(14)	0.0394(4)
H11A	0.2733	0.2555	0.2277	0.059*
H11B	0.1775	0.3554	0.2953	0.059*
H11C	0.1319	0.3413	0.1774	0.059*
C12	−0.1317(2)	0.22533(16)	0.22596(12)	0.0289(4)
H12A	−0.1305	0.2824	0.2915	0.035*
H12B	−0.1582	0.2841	0.1754	0.035*
C13	0.0248(2)	0.06932(17)	0.12553(11)	0.0264(3)
H13A	0.0018	0.1199	0.0699	0.032*
H13B	0.1292	0.0261	0.1244	0.032*
C14	−0.2596(2)	0.02433(17)	0.11254(11)	0.0256(3)
H14	−0.2770	0.0813	0.0580	0.031*
C15	−0.39533(19)	−0.08971(17)	0.09359(11)	0.0256(3)
C16	−0.3986(2)	−0.20654(18)	0.01790(12)	0.0307(4)
H16	−0.3157	−0.2133	−0.0192	0.037*
C17	−0.5236(2)	−0.31253(18)	−0.00267(13)	0.0342(4)
H17	−0.5262	−0.3896	−0.0538	0.041*
C18	−0.6441(2)	−0.30185(18)	0.05391(14)	0.0340(4)
C19	−0.6447(2)	−0.18760(19)	0.12889(13)	0.0333(4)
H19	−0.7273	−0.1821	0.1663	0.040*
C20	−0.5206(2)	−0.08110(18)	0.14776(12)	0.0297(4)
H20	−0.5211	−0.0028	0.1974	0.036*

Experimental details

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

Comment

The ketal compounds, which have applications in fragrance and flavors and a protection of carbonyl or synthetic intermediate, have attracted much attention.

The title compound was obtained by the reaction of 2-(4-chlorophenyl)-5-methyl-1,3-dioxane-5-carboxylic acid with $[NiL](ClO_4)_2$. Single crystal X-ray diffraction analyses reveal that the asymmetric unit of the title structure contains one half of a cation $[NiL]^{2+}$ and one anion $[C_{12}H_{12}O_4Cl]^-$, similar to reported structures [5, 6]. Each Ni(II) lies on an inversion center, and is coordinated with four nitrogen atoms of L in the equatorial plane and two oxygen atoms of 2-(4-chlorophenyl)-5-methyl-1,3-dioxane-5-carboxylato ligands in axial positions. The Ni—N bond lengths [2.0745(12)–2.1046(12) Å] are slightly shorter than the Ni—O bond lengths [2.1143(10) Å].

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