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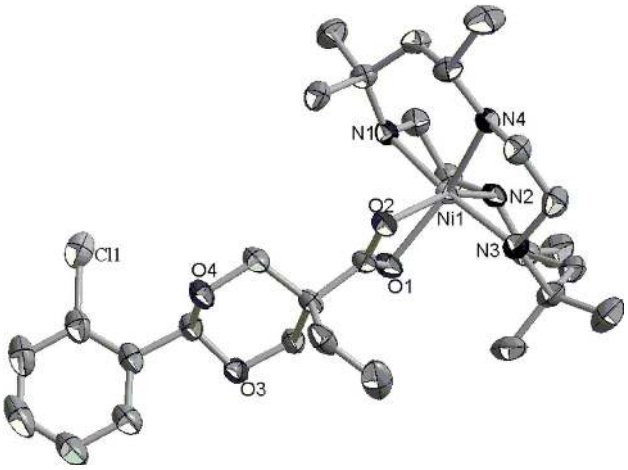
Crystal structure of [(2-(2-chlorophenyl)-5-ethyl-1,3-dioxane-5-carboxylato-κ^2*O*,*O*′) (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-κ^4*N*,*N*′,*N*″,*N*‴)]nickel(II) perchlorate, $C_{29}H_{50}Cl_2N_4NiO_8$



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Abstract

$C_{29}H_{50}Cl_2N_4NiO_8$, orthorhombic, *Pbca* (no. 61), $a = 20.601(3)$ Å, $b = 13.5059(16)$ Å, $c = 25.015(3)$ Å, $Z = 8$, $V = 6960.3(15)$ Å^3, $R_{gt}(F) = 0.0495$, $wR_{ref}(F^2) = 0.1652$, $T = 296(2)$ K.

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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 = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) was added to a solution of 4-(2-chlorophenyl)-5-ethyl-1,3-dioxane-5-carboxylic acid (0.270 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. Anal. Calcd. for $C_{29}H_{50}Cl_2N_4NiO_8$: C, 48.89; H, 7.08; N, 7.86%. Found: C, 48.57; H, 7.45; N, 7.72%. IR data (cm^{-1}, KBr): 3448(m), 3255(s), 2970(m), 1543(s), 1450(s), 1095(s).

Table 1: Data collection and handling.

Crystal:	Blue prism
Size:	0.45 × 0.36 × 0.21 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.76 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω
θ_{max}, completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	68922, 7940, 0.043
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5121
$N(param)_{refined}$:	404
Programs:	Bruker [1], SHELX [2, 3], Diamond [4]

Experimental details

The structure was solved using direct methods. All the hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations. The U_{iso} values of hydrogen atoms of methyl groups were set to $1.5U_{eq}$(C) and other hydrogen atoms were set to $1.2U_{eq}$(C, N).

Comment

A subject of interest are ketal compounds because of their application in fragrance and flavors as well as a protection of carbonyl or synthetic intermediate [5]. A new compound was synthesized by the reaction of 4-(2-chlorophenyl)-5-ethyl-1,3-dioxane-5-carboxylic acid with $[NiL](ClO_4)_2$. Some similar structures have been reported [6, 7]. X-ray crystal structural analysis reveals that the asymmetric unit of the title structure contains one cation $[Ni(C_{16}H_{36}N_4)(C_{13}H_{14}O_4Cl)]^+$, one anion $[ClO_4]^-$. The central Ni(II) atom achieves a distorted six-coordinate octahedral coordination geometry by coordination with four nitrogen atoms from L, plus two oxygen atoms from the carboxylato ligand. The Ni—N bond lengths

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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}
Ni1	0.07228(2)	0.58462(3)	0.33798(2)	0.04583(13)
Cl1	−0.23311(6)	0.22472(12)	0.42366(7)	0.1190(5)
Cl2	0.86096(5)	0.35662(7)	0.27524(4)	0.0679(3)
O1	0.05452(13)	0.43057(16)	0.34505(8)	0.0589(6)
O2	0.04276(11)	0.52420(15)	0.41603(8)	0.0551(5)
O3	−0.02306(11)	0.18131(15)	0.41468(9)	0.0583(5)
O4	−0.08557(12)	0.28839(17)	0.46531(9)	0.0629(6)
O5	0.8510(3)	0.4256(3)	0.31369(19)	0.161(2)
O6	0.9001(3)	0.2809(3)	0.2912(2)	0.185(3)
O7	0.8079(3)	0.3170(4)	0.2537(3)	0.235(3)
O8	0.8804(4)	0.4065(5)	0.2312(3)	0.233(3)
N1	−0.02353(12)	0.60130(19)	0.30438(10)	0.0514(6)
H1C	−0.0445	0.5367	0.3088	0.062*
N2	0.10240(13)	0.58006(18)	0.25839(10)	0.0519(6)
H2C	0.1127	0.6480	0.2475	0.062*
N3	0.17097(13)	0.5817(2)	0.36756(11)	0.0593(7)
H3A	0.1686	0.5492	0.4025	0.071*
N4	0.07706(12)	0.73478(19)	0.35831(10)	0.0513(6)
H4D	0.0927	0.7707	0.3268	0.062*
C1	−0.01236(17)	0.6121(3)	0.24611(13)	0.0619(8)
H1A	−0.0039	0.6810	0.2377	0.074*
H1B	−0.0509	0.5917	0.2267	0.074*
C2	0.04454(18)	0.5496(3)	0.22909(13)	0.0638(9)
H2A	0.0354	0.4803	0.2362	0.077*
H2B	0.0518	0.5572	0.1910	0.077*
C3	0.16033(18)	0.5174(3)	0.24631(14)	0.0634(9)
H3	0.1504	0.4492	0.2569	0.076*
C4	0.1767(2)	0.5174(4)	0.18631(16)	0.0940(14)
H4A	0.1401	0.4935	0.1664	0.141*
H4B	0.2134	0.4752	0.1800	0.141*
H4C	0.1869	0.5836	0.1751	0.141*
C5	0.21891(18)	0.5514(3)	0.27790(14)	0.0679(9)
H5A	0.2216	0.6229	0.2745	0.081*
H5B	0.2572	0.5241	0.2608	0.081*
C6	0.22297(18)	0.5266(3)	0.33709(14)	0.0712(10)
C7	0.2918(2)	0.5560(4)	0.3570(2)	0.1029(16)
H7A	0.3005	0.6235	0.3475	0.154*
H7B	0.3235	0.5136	0.3408	0.154*
H7C	0.2938	0.5489	0.3952	0.154*
C8	0.2127(2)	0.4163(3)	0.34691(18)	0.0925(15)
H8A	0.2215	0.4014	0.3837	0.139*
H8B	0.2415	0.3790	0.3244	0.139*
H8C	0.1686	0.3992	0.3387	0.139*
C9	0.18722(18)	0.6858(3)	0.37897(17)	0.0749(10)
H9A	0.2029	0.7175	0.3467	0.090*
H9B	0.2214	0.6886	0.4056	0.090*
C10	0.12841(17)	0.7397(3)	0.39924(15)	0.0678(9)
H10A	0.1133	0.7094	0.4321	0.081*
H10B	0.1393	0.8082	0.4066	0.081*
C11	0.01622(17)	0.7841(3)	0.37629(14)	0.0634(9)
H11	0.0014	0.7517	0.4092	0.076*
C12	0.0279(3)	0.8943(3)	0.3882(2)	0.1041(17)
H12A	0.0586	0.9006	0.4169	0.156*
H12B	−0.0124	0.9249	0.3984	0.156*
H12C	0.0446	0.9263	0.3569	0.156*
C13	−0.03669(18)	0.7746(3)	0.33446(15)	0.0663(9)
H13A	−0.0180	0.7932	0.3003	0.080*
H13B	−0.0699	0.8232	0.3428	0.080*
C14	−0.07046(16)	0.6752(3)	0.32693(15)	0.0605(8)
C15	−0.09447(19)	0.6337(3)	0.37986(16)	0.0769(11)
H15A	−0.1221	0.5777	0.3733	0.115*
H15B	−0.1185	0.6838	0.3986	0.115*
H15C	−0.0580	0.6134	0.4011	0.115*
C16	−0.12934(19)	0.6906(4)	0.29010(19)	0.0870(12)
H16A	−0.1159	0.7250	0.2584	0.131*
H16B	−0.1616	0.7289	0.3084	0.131*
H16C	−0.1472	0.6274	0.2804	0.131*
C17	0.03906(16)	0.4409(2)	0.39375(12)	0.0505(7)
C18	0.01431(16)	0.3517(2)	0.42517(11)	0.0509(7)
C19	0.0551(2)	0.3340(3)	0.47533(15)	0.0747(11)
H19A	0.0504	0.3908	0.4987	0.090*
H19B	0.0378	0.2769	0.4940	0.090*
C20	0.1259(2)	0.3171(5)	0.4657(2)	0.118(2)
H20A	0.1314	0.2649	0.4400	0.178*
H20B	0.1466	0.2987	0.4987	0.178*
H20C	0.1453	0.3767	0.4522	0.178*
C21	0.01120(16)	0.2610(2)	0.38882(13)	0.0549(7)
H21A	−0.0107	0.2783	0.3558	0.066*
H21B	0.0549	0.2397	0.3800	0.066*
C22	−0.05567(19)	0.3745(2)	0.44283(14)	0.0626(9)
H22A	−0.0553	0.4273	0.4691	0.075*
H22B	−0.0807	0.3969	0.4123	0.075*
C23	−0.08634(16)	0.2119(2)	0.42709(13)	0.0553(8)
H23	−0.1079	0.2354	0.3945	0.066*
C24	−0.12350(18)	0.1257(3)	0.44969(13)	0.0610(8)
C25	−0.1910(2)	0.1249(3)	0.44835(16)	0.0792(11)
C26	−0.2255(3)	0.0425(4)	0.4661(2)	0.1051(16)
H26	−0.2706	0.0421	0.4648	0.126*
C27	−0.1926(4)	−0.0377(4)	0.4854(2)	0.118(2)
H27	−0.2157	−0.0929	0.4969	0.142*
C28	−0.1253(3)	−0.0383(4)	0.4882(2)	0.1082(17)
H28	−0.1034	−0.0927	0.5020	0.130*
C29	−0.0915(2)	0.0438(3)	0.46994(17)	0.0804(11)
H29	−0.0464	0.0438	0.4714	0.096*

[2.086(3)−2.164(3) Å] are slightly shorter than the Ni−O bond lengths [2.119(2) and 2.202(2) Å]. Neighbouring cations and anions are connected by hydrogen bond between the oxygen atom from anion $[ClO_4]^-$ and nitrogen atom from cation $[Ni(C_{16}H_{36}N_4)(C_{13}H_{14}O_4Cl)]^+$.

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