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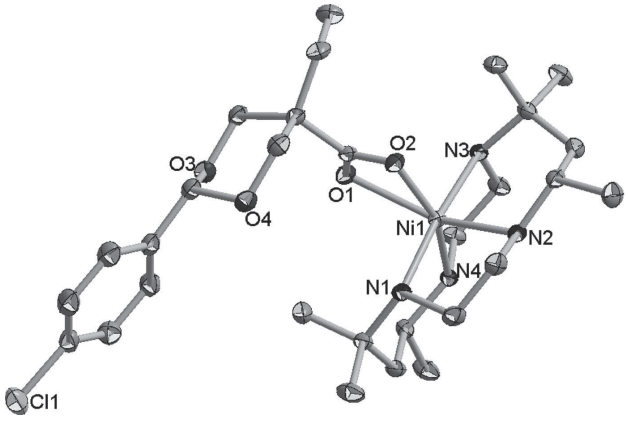
Crystal structure of (4-(4-chlorophenyl)-5-ethyl-1,3-dioxane-5-carboxylato-κ^2*O*,*O*′)-(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-κ^4*N*,*N*′,*N*″,*N*‴)nickel(II) perchlorate monohydrate, $C_{29}H_{52}Cl_2N_4NiO_9$



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Abstract

$C_{29}H_{52}Cl_2N_4NiO_9$, monoclinic, $P2_1/n$ (no. 14), $a =$ 10.8347(19) Å, $b = 14.502(3)$ Å, $c = 21.731(4)$ Å, $\beta = 93.344(2)°$, $V = 3408.6(10)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0360$, $wR_{ref}(F^2) = 0.1009$, $T = 296(2)$ K.

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The crystal structure is shown in the figure. Hydrogen atoms are omitted for clarity. Tables 1 and 2 contain details on crystal structure and measurement conditions and a 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-(4-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

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Table 1: Data collection and handling.

Crystal:	Prism, blue
Size:	0.45 × 0.42 × 0.30 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.78 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
θ_{max}, completeness:	27.5°, >97% (up to 25.2°, >99%)
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	37399, 7623, 0.019
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6625
$N(param)_{refined}$:	419
Programs:	Bruker programs [1], SHELX [2, 3]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.26359(2)	0.52040(2)	0.16501(2)	0.02486(8)
Cl1	0.82771(6)	0.82560(4)	0.19051(3)	0.05458(16)
Cl2	−0.34104(7)	0.02911(5)	0.00498(4)	0.0705(2)
N1	0.09651(14)	0.51940(11)	0.10828(7)	0.0305(3)
H1C	0.1159	0.4846	0.0714	0.037*
N2	0.27869(14)	0.65691(10)	0.13539(7)	0.0295(3)
H2C	0.2389	0.6962	0.1651	0.035*
N3	0.42254(14)	0.53193(11)	0.22709(7)	0.0294(3)
H3A	0.4565	0.4695	0.2313	0.035*
N4	0.16406(13)	0.53492(10)	0.24460(7)	0.0265(3)
H4D	0.1503	0.6012	0.2499	0.032*
O1	0.29848(12)	0.36685(9)	0.16072(6)	0.0344(3)
O1W	0.34802(17)	0.24713(12)	0.25914(8)	0.0539(4)
H1WB	0.322(2)	0.2800(17)	0.2283(9)	0.065*
H1WA	0.4210(13)	0.2635(19)	0.2701(11)	0.065*
O2	0.34195(13)	0.46143(9)	0.08699(6)	0.0351(3)
O3	0.21761(13)	0.18276(10)	0.08573(6)	0.0397(3)
O4	0.17587(14)	0.28523(10)	0.00549(6)	0.0389(3)
O5	0.7527(2)	0.8441(2)	0.23994(11)	0.0928(7)
O6	0.9437(2)	0.8692(2)	0.19691(14)	0.1018(9)
O7	0.7664(3)	0.8636(4)	0.13739(14)	0.1602(18)
O8	0.8442(4)	0.7349(2)	0.1815(3)	0.203(3)
C1	0.07826(19)	0.61579(15)	0.08696(10)	0.0403(5)
H1A	0.0360	0.6506	0.1175	0.048*
H1B	0.0274	0.6165	0.0487	0.048*
C2	0.2013(2)	0.65943(15)	0.07704(9)	0.0397(5)
H2A	0.2422	0.6263	0.0452	0.048*
H2B	0.1895	0.7228	0.0636	0.048*
C3	0.40550(18)	0.69357(13)	0.12869(9)	0.0335(4)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H3	0.4454	0.6557	0.0982	0.040*
C4	0.4040(2)	0.79333(16)	0.10613(12)	0.0501(6)
H4A	0.3595	0.7969	0.0667	0.075*
H4B	0.4873	0.8142	0.1024	0.075*
H4C	0.3642	0.8316	0.1351	0.075*
C5	0.48196(19)	0.68724(14)	0.18932(9)	0.0362(4)
H5A	0.4328	0.7123	0.2213	0.043*
H5B	0.5532	0.7272	0.1865	0.043*
C6	0.52901(17)	0.59238(14)	0.21085(9)	0.0341(4)
C7	0.59570(19)	0.54337(16)	0.16040(11)	0.0437(5)
H7A	0.6347	0.4886	0.1769	0.066*
H7B	0.6573	0.5836	0.1451	0.066*
H7C	0.5372	0.5271	0.1273	0.066*
C8	0.62207(19)	0.60658(18)	0.26621(11)	0.0472(5)
H8A	0.5863	0.6459	0.2959	0.071*
H8B	0.6959	0.6346	0.2525	0.071*
H8C	0.6422	0.5480	0.2848	0.071*
C9	0.37464(17)	0.55461(15)	0.28784(9)	0.0351(4)
H9A	0.3634	0.6208	0.2911	0.042*
H9B	0.4340	0.5354	0.3205	0.042*
C10	0.25306(17)	0.50647(15)	0.29512(9)	0.0340(4)
H10A	0.2648	0.4402	0.2940	0.041*
H10B	0.2213	0.5225	0.3345	0.041*
C11	0.04105(17)	0.48930(13)	0.24930(9)	0.0316(4)
H11	0.0537	0.4224	0.2503	0.038*
C12	−0.0210(2)	0.51756(18)	0.30777(10)	0.0472(5)
H12A	0.0344	0.5062	0.3431	0.071*
H12B	−0.0952	0.4823	0.3112	0.071*
H12C	−0.0411	0.5820	0.3058	0.071*
C13	−0.04677(17)	0.51258(14)	0.19390(9)	0.0336(4)
H13A	−0.0513	0.5792	0.1907	0.040*
H13B	−0.1285	0.4910	0.2029	0.040*
C14	−0.01813(17)	0.47499(14)	0.13036(9)	0.0343(4)
C15	−0.1293(2)	0.4952(2)	0.08481(11)	0.0511(6)
H15A	−0.1509	0.5592	0.0872	0.077*
H15B	−0.1985	0.4581	0.0952	0.077*
H15C	−0.1078	0.4808	0.0437	0.077*
C16	0.0032(2)	0.37139(16)	0.13215(12)	0.0488(5)
H16A	0.0133	0.3492	0.0911	0.073*
H16B	−0.0667	0.3416	0.1488	0.073*
H16C	0.0763	0.3580	0.1577	0.073*
C17	0.33519(16)	0.38038(13)	0.10742(8)	0.0295(4)
C18	0.37371(18)	0.30143(13)	0.06555(9)	0.0333(4)
C19	0.5133(2)	0.31096(17)	0.05644(12)	0.0490(5)
H19A	0.5352	0.2690	0.0241	0.059*
H19B	0.5295	0.3732	0.0426	0.059*
C20	0.5958(2)	0.2913(2)	0.11373(15)	0.0651(7)
H20A	0.5715	0.3297	0.1469	0.098*
H20B	0.6802	0.3042	0.1055	0.098*
H20C	0.5880	0.2277	0.1250	0.098*
C21	0.34589(19)	0.20577(14)	0.09103(10)	0.0377(4)
H21A	0.3917	0.1601	0.0691	0.045*
H21B	0.3745	0.2033	0.1341	0.045*
C22	0.3028(2)	0.31099(16)	0.00260(9)	0.0407(5)
H22A	0.3076	0.3744	−0.0113	0.049*
H22B	0.3413	0.2722	−0.0272	0.049*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C23	0.1700(2)	0.19155(14)	0.02419(9)	0.0377(4)
H23	0.2203	0.1543	−0.0024	0.045*
C24	0.0396(2)	0.15631(14)	0.01918(9)	0.0379(4)
C25	−0.0079(2)	0.11880(17)	−0.03608(11)	0.0491(5)
H25	0.0396	0.1195	−0.0704	0.059*
C26	−0.1247(2)	0.08056(18)	−0.04062(12)	0.0551(6)
H26	−0.1558	0.0556	−0.0778	0.066*
C27	−0.1944(2)	0.07955(15)	0.00986(12)	0.0462(5)
C28	−0.1507(2)	0.11636(17)	0.06520(12)	0.0497(5)
H28	−0.1990	0.1158	0.0992	0.060*
C29	−0.0330(2)	0.15441(16)	0.06931(10)	0.0445(5)
H29	−0.0025	0.1792	0.1066	0.053*

amount of water. After a few days, blue crystals were separated in ∼32% yield. Anal. Calcd. for $C_{29}H_{52}Cl_2N_4NiO_9$: C, 47.69; H, 7.17; N, 7.67%. Found: C, 47.25; H, 7.51; N, 7.89%. **IR** data (cm^{-1}, KBr): 3456(m), 3209(s), 2962(m), 1545(s), 1450(s), 1090(s).

Experimental details

All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the final stage of refinement. The U_{iso} (H) values 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

Ketal compounds are subjects of great interest because they are usually used as a protection of carbonyl or synthetic intermediates [4], and have been widely applied in fragrance and flavors as well as a new type of spices.

X-ray crystal structural analysis reveals that the title compound contains one complex cation $[Ni(C_{16}H_{36}N_4)(C_{13}H_{14}O_4Cl)]^+$, one anion $[ClO_4]^-$, and one water molecule. Each Ni(II) ion lies on a general position of the monoclinic space group and is coordinated by four macrocyclic nitrogen atoms of L in a folded conformation and two carboxylate oxygen atoms of the anionic 4-(chlorophenyl)-5-ethyl-1,3-dioxane-5-carboxylato ligand. The Ni-N bond lengths [2.090(6)–2.131(6) Å] are slightly shorter than the Ni-O bond lengths [2.120(4) and 2.261(4) Å]. Neighbouring cations and anions are discrete, connected to each other through hydrogen bonds between the carboxylate oxygen atom of 4-(chlorophenyl)-5-ethyl-1,3-dioxane-5-carboxylato ligand and water and nitrogen atom of adjacent cation, forming a one-dimensional chain.

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