Guang-Chuan Ou*, Guo-Kai Jia, Fei Zeng, Ying-zhi Tan and Qiong Wang
Crystal structure of (2-(chlorophenyl)-5-methyl-1,3-dioxane-5-carboxylato- $\kappa^2 O, O'$)(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane- $\kappa^4 N, N', N'', N'''$)nickel(II) perchlorate monohydrate, $\text{Ni}(\text{C}_{16}\text{H}_{36}\text{N}_4)(\text{C}_{12}\text{H}_{12}\text{O}_4\text{Cl})\text{ClO}_4 \cdot \text{H}_2\text{O}$

Table 1: Data collection and handling.

Crystal:	Prism, blue
Size:	$0.45 \times 0.23 \times 0.20$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.79 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
θ_{max} , completeness:	27.6° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	37530, 7665, 0.029
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6114
$N(\text{param})_{\text{refined}}$:	410
Programs:	Bruker programs [1], SHELX [2, 3], Diamond [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.64292(2)	0.151289(9)	−0.02413(2)	0.02668(8)
Cl1	0.84508(6)	0.19698(2)	0.66895(5)	0.04612(15)
Cl2	0.75668(9)	0.00377(4)	0.59676(6)	0.0854(3)
N1	0.79790(18)	0.09646(7)	0.00534(16)	0.0375(4)
N2	0.60361(17)	0.12316(6)	−0.18222(14)	0.0311(4)
N3	0.49349(17)	0.20762(7)	−0.06464(14)	0.0321(4)
N4	0.77366(17)	0.21027(7)	−0.03629(14)	0.0323(4)
O1	0.63312(15)	0.16210(6)	0.13897(12)	0.0358(3)
O1W	0.3453(3)	0.01373(10)	0.9597(2)	0.0768(6)
O2	0.53077(15)	0.09638(6)	0.05509(12)	0.0370(3)
O3	0.71756(17)	0.08111(6)	0.35529(13)	0.0433(4)
O4	0.57426(17)	0.02152(6)	0.25934(14)	0.0439(4)
O5	0.7573(3)	0.22473(12)	0.7206(2)	0.0948(9)
O6	0.9019(5)	0.22828(16)	0.6117(4)	0.198(2)
O7	0.7763(4)	0.16257(18)	0.5995(5)	0.197(3)
O8	0.9394(4)	0.17401(19)	0.7460(3)	0.172(2)
C1	0.7998(3)	0.07412(10)	−0.1014(2)	0.0502(6)
H1A	0.8369	0.0401	−0.0918	0.060*
H1B	0.8553	0.0946	−0.1376	0.060*
H1C	0.7689	0.0712	0.0437	0.045*
H1WA	0.382(3)	−0.0013(12)	0.912(2)	0.092*
H1WB	0.400(3)	0.0382(10)	0.987(3)	0.092*
C2	0.6613(3)	0.07187(9)	−0.1698(2)	0.0457(6)
H2A	0.6635	0.0580	−0.2405	0.055*
H2B	0.6071	0.0498	−0.1358	0.055*
H2C	0.6527	0.1418	−0.2198	0.037*
C3	0.4656(2)	0.12269(9)	−0.24732(18)	0.0366(5)
H3	0.4142	0.0984	−0.2143	0.044*
H3A	0.4676	0.2144	−0.0017	0.039*
C4	0.4615(3)	0.10565(10)	−0.3639(2)	0.0515(6)
H4A	0.5157	0.1279	−0.3962	0.077*

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Abstract

$\text{C}_{28}\text{H}_{50}\text{Cl}_2\text{N}_4\text{NiO}_9$, monoclinic, $P2_1/n$, $a = 10.333(4)$ Å, $b = 26.305(9)$ Å, $c = 12.640(5)$ Å, $\beta = 102.421(4)^\circ$, $V = 3355(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0391$, $wR_{\text{ref}}(F^2) = 0.1090$, $T = 296(2)$ K.

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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 $[\text{NiL}](\text{ClO}_4)_2$ (0.270 g, 0.5 mmol) ($L = \text{rac-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane}$) was added to a solution of 2-(chloro-

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Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H4B	0.3718	0.1069	−0.4049	0.077*
H4C	0.4942	0.0715	−0.3636	0.077*
H4D	0.7823	0.2112	−0.1064	0.039*
C5	0.4002(2)	0.17467(9)	−0.24935(18)	0.0403(5)
H5A	0.3181	0.1734	−0.3036	0.048*
H5B	0.4573	0.1990	−0.2747	0.048*
C6	0.3679(2)	0.19621(9)	−0.14575(18)	0.0374(5)
C7	0.2830(3)	0.24402(11)	−0.1753(2)	0.0542(7)
H7A	0.2713	0.2605	−0.1103	0.081*
H7B	0.1980	0.2346	−0.2184	0.081*
H7C	0.3264	0.2668	−0.2158	0.081*
C8	0.2888(2)	0.15861(11)	−0.0933(2)	0.0492(6)
H8A	0.3408	0.1286	−0.0723	0.074*
H8B	0.2089	0.1497	−0.1441	0.074*
H8C	0.2668	0.1739	−0.0304	0.074*
C9	0.5625(2)	0.25402(9)	−0.0887(2)	0.0429(5)
H9A	0.5130	0.2838	−0.0757	0.052*
H9B	0.5682	0.2540	−0.1643	0.052*
C10	0.6989(3)	0.25588(9)	−0.0183(2)	0.0445(6)
H10A	0.7445	0.2860	−0.0351	0.053*
H10B	0.6931	0.2577	0.0572	0.053*
C11	0.9096(2)	0.20960(10)	0.03253(19)	0.0425(5)
H11	0.9029	0.2144	0.1081	0.051*
C12	0.9933(3)	0.25259(12)	0.0023(3)	0.0648(8)
H12A	1.0028	0.2481	−0.0710	0.097*
H12B	1.0791	0.2522	0.0501	0.097*
H12C	0.9507	0.2845	0.0088	0.097*
C13	0.9800(2)	0.15931(10)	0.0243(2)	0.0461(6)
H13A	0.9769	0.1532	−0.0519	0.055*
H13B	1.0724	0.1639	0.0592	0.055*
C14	0.9325(2)	0.11101(10)	0.0703(2)	0.0466(6)
C15	0.9219(3)	0.11795(13)	0.1877(2)	0.0591(7)
H15A	0.8534	0.1422	0.1913	0.089*
H15B	1.0048	0.1301	0.2295	0.089*
H15C	0.9007	0.0860	0.2164	0.089*
C16	1.0338(3)	0.06865(13)	0.0662(3)	0.0728(9)
H16A	1.0003	0.0369	0.0866	0.109*
H16B	1.1158	0.0766	0.1155	0.109*
H16C	1.0487	0.0660	−0.0060	0.109*
C17	0.5631(2)	0.12332(8)	0.13939(17)	0.0312(4)
C18	0.5107(2)	0.11112(9)	0.24052(18)	0.0380(5)
C19	0.3933(3)	0.14688(11)	0.2405(3)	0.0598(8)
H19A	0.3288	0.1429	0.1739	0.090*
H19B	0.4240	0.1814	0.2470	0.090*
H19C	0.3537	0.1387	0.3004	0.090*
C21	0.6182(3)	0.11968(9)	0.34236(19)	0.0459(6)
H21A	0.6590	0.1526	0.3381	0.055*
H21B	0.5783	0.1198	0.4052	0.055*
C22	0.4651(2)	0.05629(9)	0.2406(2)	0.0448(6)
H22A	0.4148	0.0519	0.2965	0.054*
H22B	0.4070	0.0486	0.1714	0.054*
C23	0.6603(2)	0.03294(9)	0.35933(19)	0.0418(5)
H23	0.6095	0.0328	0.4165	0.050*
C24	0.7670(2)	−0.00602(9)	0.3851(2)	0.0434(5)
C25	0.8165(3)	−0.02216(11)	0.4905(2)	0.0511(6)
C26	0.9149(3)	−0.05859(13)	0.5148(3)	0.0697(9)
H26	0.9467	−0.0686	0.5862	0.084*
C27	0.9649(3)	−0.07964(13)	0.4339(3)	0.0787(10)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H27	1.0309	−0.1042	0.4500	0.094*
C28	0.9184(3)	−0.06478(14)	0.3290(3)	0.0760(10)
H28	0.9530	−0.0792	0.2738	0.091*
C29	0.8203(3)	−0.02842(12)	0.3047(2)	0.0597(7)
H29	0.7893	−0.0187	0.2330	0.072*

phenyl)-5-methyl-1,3-dioxane-5-carboxylic acid (0.256 g, 1.0 mmol) and NaOH (0.04 g, 1.0 mmol) in the minimum amount of water. After a few days, blue crystals were separated in ~ 30% yield. Anal. calcd. for C₂₈H₅₀Cl₂N₄NiO₉: C, 46.95; H, 7.03; N, 7.82%. Found: C, 46.56; H, 7.52; N, 7.47%. IR data (cm^{−1}, KBr): 3454(s), 3240(w), 1646(s), 1466(s), 1111(s).

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Discussion

Ketals have a subject of interest because they are usually used as a protection of carbonyl or synthetic intermediate [5], and have been widely applied in fragrance and flavors as well as a new type of spices.

Crystal structural analysis reveals that the title complex contains one cation [Ni(C₁₆H₃₆N₄)(C₁₂H₁₂O₄Cl)]⁺ (cf. the figure), one anion [ClO₄][−], and one water molecule. Each Ni(II) ion is coordinated with four macrocyclic nitrogen atoms of L in a folded conformation and two carboxylate oxygen atoms of 2-(chlorophenyl)-5-methyl-1,3-dioxane-5-carboxylate in *cis*-position. Neighbouring ions and molecules are connected to each other through hydrogen bonds.

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