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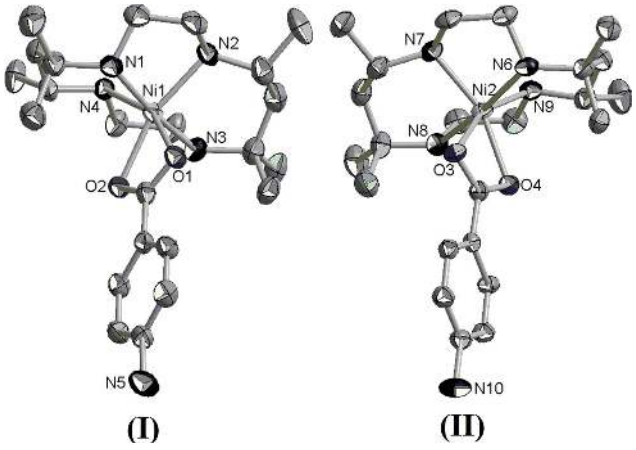
Crystal structure of (4-aminobenzoato-κ^2*O*,*O′*)-[5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-κ^4*N*,*N′*,*N″*,*N‴*]nickel(II) perchlorate monohydrate, $C_{23}H_{44}ClN_5NiO_7$



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Abstract

$C_{23}H_{44}ClN_5NiO_7$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 14.4994(16)$ Å, $b = 19.799(2)$ Å, $c = 20.040(2)$ Å, $V = 5752.9(11)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0409$, $wR_{ref}(F^2) = 0.1061$, $T = 173(2)$ 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

A water solution (20 mL) of 4-aminobenzoic acid (0.274 g, 2 mmol) and NaOH (0.08 g, 2 mmol) was added to a acetonitrile solution of [Ni(*rac*-L)](ClO$_4$)$_2$ (0.108 g, 2 mmol). The resulting solution was evaporated slowly at room temperature and blue crystals of the title compound were obtained after two weeks.

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Table 1: Data collection and handling.

Crystal:	Purple block
Size:	0.47 × 0.41 × 0.22 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.82 mm^{-1}
Diffractometer, scan mode:	Bruker SMART II, φ and ω
θ_{max}, completeness:	27.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	40380, 12576, 0.033
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 10129
$N(param)_{refined}$:	703
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	0.52551(4)	0.84445(3)	0.15772(3)	0.03049(13)
Ni2	0.01474(4)	0.20679(3)	0.14671(2)	0.02877(13)
Cl1	0.81142(8)	0.34881(6)	0.01360(6)	0.0419(3)
Cl2	0.92734(10)	0.80950(7)	0.02317(6)	0.0492(3)
O1	0.5100(2)	0.92534(15)	0.23006(14)	0.0365(7)
O2	0.6467(2)	0.89153(15)	0.19674(15)	0.0348(7)
O3	0.0241(2)	0.13137(14)	0.22575(13)	0.0316(6)
O4	0.1460(2)	0.17127(15)	0.17459(14)	0.0338(7)
O5	0.7488(3)	0.3334(3)	0.0676(2)	0.0765(13)
O6	0.7682(4)	0.3901(3)	−0.0323(3)	0.106(2)
O7	0.8921(3)	0.37978(19)	0.04147(19)	0.0547(10)
O8	0.8355(3)	0.2849(2)	−0.0134(3)	0.0849(15)
O9	0.8771(4)	0.8660(2)	0.0453(3)	0.0831(15)
O10	0.9122(4)	0.7536(3)	0.0662(2)	0.0943(17)
O11	0.8984(5)	0.7898(2)	−0.0408(2)	0.0956(19)
O12	1.0221(4)	0.8227(4)	0.0217(4)	0.147(3)
O1W	0.9566(3)	0.1787(2)	0.34654(17)	0.0542(9)
H1WA	1.000(3)	0.189(3)	0.374(2)	0.065*
H1WB	0.979(3)	0.154(2)	0.3155(19)	0.065*
O2W	0.7486(6)	0.9567(3)	0.0944(4)	0.122(2)
H2WA	0.725(7)	0.927(3)	0.123(3)	0.146*
H2WB	0.766(7)	0.932(3)	0.060(3)	0.146*
N1	0.4864(3)	0.77995(19)	0.23848(18)	0.0375(9)
H1C	0.4717	0.8107	0.2766	0.045*
N2	0.3879(3)	0.8342(2)	0.12748(19)	0.0385(9)
H2C	0.3861	0.7992	0.0914	0.046*
N3	0.5552(3)	0.89878(19)	0.06862(19)	0.0385(9)
H3A	0.6120	0.9256	0.0787	0.046*
N4	0.5912(3)	0.76400(18)	0.11080(18)	0.0331(8)
H4D	0.5427	0.7346	0.0905	0.040*
N5	0.7614(4)	1.1445(3)	0.3764(3)	0.0588(13)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H5E	0.821(5)	1.157(3)	0.375(3)	0.071*
H5D	0.730(5)	1.160(3)	0.405(3)	0.071*
N6	−0.0171(3)	0.27940(18)	0.22286(16)	0.0324(8)
H6A	−0.0206	0.2531	0.2654	0.039*
N7	−0.1263(2)	0.2026(2)	0.13214(17)	0.0344(8)
H7D	−0.1415	0.2295	0.0913	0.041*
N8	0.0344(3)	0.14363(19)	0.06031(17)	0.0368(9)
H8D	0.0981	0.1248	0.0647	0.044*
N9	0.0577(3)	0.28487(19)	0.08427(17)	0.0341(8)
H9C	0.0023	0.3111	0.0697	0.041*
N10	0.3382(4)	−0.0728(3)	0.3268(3)	0.0539(13)
H10E	0.395(5)	−0.074(3)	0.314(3)	0.065*
H10D	0.330(5)	−0.086(3)	0.361(3)	0.065*
C1	0.3970(4)	0.7515(3)	0.2167(3)	0.0468(12)
H1A	0.3643	0.7317	0.2555	0.056*
H1B	0.4077	0.7151	0.1837	0.056*
C2	0.3389(3)	0.8060(3)	0.1860(3)	0.0467(12)
H2A	0.2787	0.7872	0.1720	0.056*
H2B	0.3274	0.8421	0.2191	0.056*
C3	0.3434(4)	0.8963(3)	0.1007(3)	0.0486(13)
H3	0.3510	0.9333	0.1342	0.058*
C4	0.2400(4)	0.8868(4)	0.0875(4)	0.076(2)
H4A	0.2307	0.8469	0.0593	0.115*
H4B	0.2157	0.9268	0.0646	0.115*
H4C	0.2077	0.8807	0.1299	0.115*
C5	0.3913(4)	0.9181(3)	0.0357(3)	0.0498(13)
H5A	0.3943	0.8781	0.0062	0.060*
H5B	0.3508	0.9515	0.0134	0.060*
C6	0.4879(4)	0.9485(2)	0.0391(2)	0.0428(11)
C7	0.5154(5)	0.9703(3)	−0.0302(3)	0.0588(15)
H7A	0.5811	0.9820	−0.0306	0.088*
H7B	0.4790	1.0098	−0.0434	0.088*
H7C	0.5041	0.9333	−0.0616	0.088*
C8	0.4907(4)	1.0115(2)	0.0855(3)	0.0503(13)
H8A	0.4770	0.9977	0.1314	0.075*
H8B	0.4446	1.0444	0.0705	0.075*
H8C	0.5522	1.0320	0.0837	0.075*
C9	0.5850(4)	0.8462(3)	0.0208(2)	0.0463(12)
H9A	0.6204	0.8673	−0.0161	0.056*
H9B	0.5303	0.8236	0.0014	0.056*
C10	0.6442(4)	0.7952(2)	0.0561(2)	0.0415(11)
H10A	0.6643	0.7599	0.0242	0.050*
H10B	0.6999	0.8175	0.0742	0.050*
C11	0.6501(3)	0.7207(2)	0.1549(2)	0.0395(10)
H11	0.6961	0.7504	0.1776	0.047*
C12	0.7027(4)	0.6674(3)	0.1153(3)	0.0575(15)
H12A	0.6594	0.6421	0.0872	0.086*
H12B	0.7336	0.6364	0.1461	0.086*
H12C	0.7487	0.6896	0.0869	0.086*
C13	0.5922(4)	0.6864(2)	0.2085(3)	0.0445(12)
H13A	0.6302	0.6501	0.2284	0.053*
H13B	0.5395	0.6643	0.1859	0.053*
C14	0.5533(4)	0.7286(3)	0.2656(2)	0.0450(12)
C15	0.6282(4)	0.7673(3)	0.3037(3)	0.0544(14)
H15A	0.6573	0.8002	0.2738	0.082*
H15B	0.6748	0.7354	0.3200	0.082*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H15C	0.6003	0.7909	0.3416	0.082*
C16	0.5055(4)	0.6799(3)	0.3152(3)	0.0624(16)
H16A	0.4697	0.7060	0.3477	0.094*
H16B	0.5523	0.6532	0.3387	0.094*
H16C	0.4642	0.6496	0.2907	0.094*
C17	0.5971(3)	0.9314(2)	0.2312(2)	0.0339(10)
C18	0.6409(3)	0.9858(2)	0.2708(2)	0.0338(10)
C19	0.5897(3)	1.0239(2)	0.3158(2)	0.0383(11)
H19	0.5258	1.0146	0.3213	0.046*
C20	0.6303(3)	1.0752(2)	0.3527(2)	0.0432(11)
H20	0.5945	1.0995	0.3843	0.052*
C21	0.7231(3)	1.0913(2)	0.3439(2)	0.0402(11)
C22	0.7750(3)	1.0530(2)	0.2987(2)	0.0404(11)
H22	0.8385	1.0628	0.2921	0.049*
C23	0.7342(3)	1.0009(3)	0.2637(2)	0.0381(11)
H23	0.7706	0.9747	0.2340	0.046*
C24	−0.1126(3)	0.2989(3)	0.2073(2)	0.0391(11)
H24A	−0.1131	0.3303	0.1688	0.047*
H24B	−0.1401	0.3225	0.2461	0.047*
C25	−0.1681(3)	0.2373(3)	0.1911(2)	0.0396(11)
H25A	−0.1688	0.2063	0.2299	0.048*
H25B	−0.2325	0.2503	0.1809	0.048*
C26	−0.1614(3)	0.1323(2)	0.1225(2)	0.0383(11)
H26	−0.1352	0.1034	0.1587	0.046*
C27	−0.2669(4)	0.1283(3)	0.1265(3)	0.0510(13)
H27A	−0.2872	0.1414	0.1713	0.076*
H27B	−0.2868	0.0819	0.1174	0.076*
H27C	−0.2941	0.1588	0.0935	0.076*
C28	−0.1275(4)	0.1047(3)	0.0554(2)	0.0437(12)
H28A	−0.1657	0.0649	0.0443	0.052*
H28B	−0.1402	0.1395	0.0211	0.052*
C29	−0.0269(4)	0.0841(2)	0.0483(2)	0.0426(11)
C30	−0.0127(5)	0.0551(3)	−0.0224(3)	0.0599(15)
H30A	−0.0321	0.0885	−0.0556	0.090*
H30B	−0.0495	0.0139	−0.0275	0.090*
H30C	0.0527	0.0443	−0.0289	0.090*
C31	0.0000(4)	0.0295(2)	0.0987(3)	0.0520(14)
H31A	0.0648	0.0171	0.0921	0.078*
H31B	−0.0391	−0.0103	0.0922	0.078*
H31C	−0.0084	0.0469	0.1441	0.078*
C32	0.0391(3)	0.1928(2)	0.0049(2)	0.0408(11)
H32A	−0.0237	0.2088	−0.0064	0.049*
H32B	0.0656	0.1709	−0.0352	0.049*
C33	0.0983(4)	0.2515(3)	0.0255(2)	0.0411(11)
H33A	0.1612	0.2354	0.0363	0.049*
H33B	0.1029	0.2841	−0.0118	0.049*
C34	0.1232(3)	0.3318(2)	0.1185(2)	0.0372(10)
H34	0.1707	0.3037	0.1418	0.045*
C35	0.1738(5)	0.3789(3)	0.0697(3)	0.0621(17)
H35A	0.2138	0.3521	0.0406	0.093*
H35B	0.2112	0.4112	0.0949	0.093*
H35C	0.1285	0.4033	0.0426	0.093*
C36	0.0725(4)	0.3728(2)	0.1713(2)	0.0387(11)
H36A	0.0147	0.3899	0.1511	0.046*
H36B	0.1110	0.4125	0.1824	0.046*
C37	0.0477(3)	0.3367(2)	0.2366(2)	0.0364(10)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C38	0.0053(4)	0.3891(2)	0.2844(2)	0.0463(12)
H38A	−0.0473	0.4111	0.2627	0.069*
H38B	0.0518	0.4232	0.2958	0.069*
H38C	−0.0156	0.3665	0.3252	0.069*
C39	0.1330(3)	0.3065(3)	0.2698(2)	0.0413(11)
H39A	0.1158	0.2868	0.3129	0.062*
H39B	0.1791	0.3421	0.2769	0.062*
H39C	0.1590	0.2713	0.2410	0.062*
C40	0.1104(3)	0.1280(2)	0.2137(2)	0.0302(9)
C41	0.1685(3)	0.0748(2)	0.2433(2)	0.0286(9)
C42	0.1377(3)	0.0357(2)	0.2970(2)	0.0323(9)
H42	0.0773	0.0425	0.3140	0.039*
C43	0.1935(3)	−0.0123(2)	0.3255(2)	0.0365(10)
H43	0.1720	−0.0377	0.3626	0.044*
C44	0.2817(3)	−0.0238(2)	0.2999(2)	0.0377(11)
C45	0.3121(3)	0.0145(2)	0.2457(2)	0.0361(10)
H45	0.3720	0.0072	0.2280	0.043*
C46	0.2556(3)	0.0625(2)	0.2179(2)	0.0316(9)
H46	0.2768	0.0878	0.1807	0.038*

Experimental details

The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms. All hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic displacement parameters and included in the structure factor calculations in the final stage of 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

Similar to the reported structures [5, 6], the title structure documented a chelating mode for the carboxylate ion. The ortho amino forms hydrogen bonds with the carboxylate oxygen. The benzoate has a para amino unit that also engages in hydrogen bonding.

In detail, the X-ray crystal structural analysis displays that there are two crystallographically independent molecules of the title compound in an asymmetric unit plus two perchlorate counter anions and two water molecules (see the Figure; only the two cationic metal complexes are shown). The macrocyclic ligand adopts a SS and RR conformation in two molecules, respectively. The Ni(II) atom displays a six-coordinate octahedral geometry by coordination with four nitrogen atoms from the macrocycle in a folded conformation and the carboxylate anion in *cis*-position. The cation, anion and lattice water molecules are linked by N—H···O and O—H···O hydrogen bonds into a three-dimensional structure.

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