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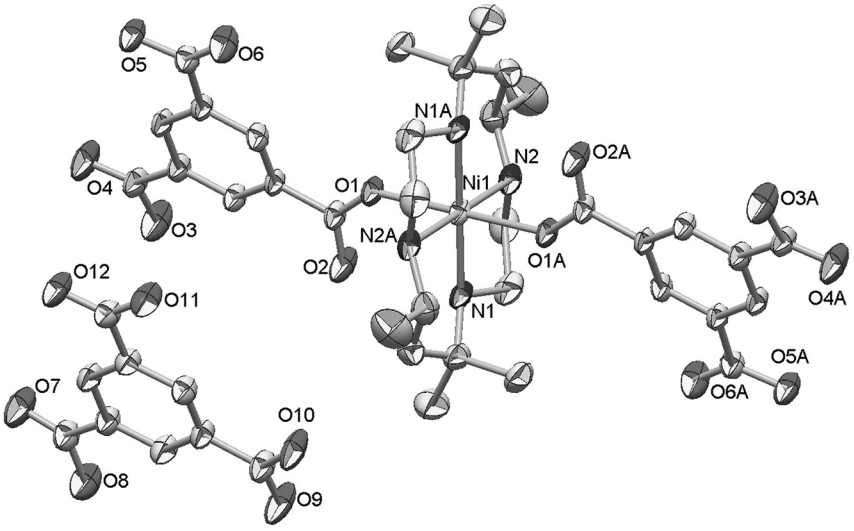
Crystal structure of bis(benzene-1 carboxylato-*O* 3,5-carboxyl-κ^1O)-[(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-κ^4*N*,*N*′,*N*″,*N*‴) nickel(II) − benzene-1,3,5-tricarboxylic acid − water (1/2/4), $C_{52}H_{66}N_4NiO_{28}$



https://doi.org/10.1515/ncrs-2023-0389
Received August 31, 2023; accepted October 20, 2023;
published online November 1, 2023

Abstract

$C_{52}H_{66}N_4NiO_{28}$, triclinic, $P\bar{1}$ (no. 2), a = 11.292(6) Å, b = 11.670(6) Å, c = 12.165(6) Å, α = 81.872(6)°, β = 67.036(5)°, γ = 75.624(6)°, V = 1428.1(12) Å^3, Z = 1, $R_{gt}(F)$ = 0.0439, $wR_{ref}(F^2)$ = 0.1216, T = 296(2) K.

CCDC no.: 2302378

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.45 × 0.28 × 0.20 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.43 mm^{-1}
Diffractometer, scan mode:	Bruker SMART II, φ and ω
θ_{max}, completeness:	27.4°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	15,999, 6262, 0.025
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 5008
$N(param)_{refined}$:	405
Programs:	Bruker [1], SHELX [2, 3], Diamond [4]

1 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 methanol solution of benzene-1,3,5-tricarboxylic acid (BTC, 0.315 g, 1.5 mmol). The resulting solution was evaporated slowly at room temperature to give crystals of the title compound after 2 weeks.

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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}
C1	0.66264 (18)	0.35588 (16)	0.75662 (16)	0.0339 (4)
C2	0.9167 (2)	0.20218 (18)	0.34066 (17)	0.0426 (5)
C3	0.62771 (19)	0.60818 (17)	0.40096 (17)	0.0373 (4)
C4	0.70477 (18)	0.37100 (16)	0.62174 (15)	0.0320 (4)
C5	0.79005 (19)	0.28096 (16)	0.54685 (16)	0.0344 (4)
H5	0.824435	0.209833	0.579530	0.041*
C6	0.82410 (19)	0.29671 (16)	0.42359 (16)	0.0349 (4)
C7	0.77190 (19)	0.40215 (16)	0.37390 (16)	0.0348 (4)
H7	0.793630	0.412135	0.291641	0.042*
C8	0.68708 (18)	0.49255 (16)	0.44781 (16)	0.0324 (4)
C9	0.65493 (18)	0.47633 (16)	0.57060 (16)	0.0335 (4)
H9	0.598828	0.537325	0.619609	0.040*
C19	0.6365 (2)	0.30696 (19)	1.1086 (2)	0.0501 (6)
H19A	0.679127	0.224145	1.112072	0.060*
H19B	0.595238	0.334277	1.189308	0.060*
C20	0.7366 (2)	0.37871 (19)	1.0326 (2)	0.0493 (5)
H20A	0.801340	0.373328	1.068052	0.059*
H20B	0.781831	0.347791	0.953443	0.059*
C21	0.7514 (2)	0.5797 (2)	0.9319 (2)	0.0470 (5)
H21	0.768627	0.553808	0.852924	0.056*
C22	0.6738 (2)	0.7081 (2)	0.9414 (2)	0.0505 (6)
H22A	0.737063	0.758763	0.907535	0.061*
H22B	0.629514	0.723319	1.025684	0.061*
C23	0.8831 (3)	0.5696 (3)	0.9434 (3)	0.0796 (9)
H23A	0.868710	0.600545	1.017643	0.119*
H23B	0.936033	0.613989	0.878208	0.119*
H23C	0.927701	0.487931	0.941476	0.119*
C24	0.4296 (2)	0.25161 (17)	1.11695 (18)	0.0450 (5)
C25	0.3666 (3)	0.2711 (2)	1.25008 (18)	0.0591 (6)
H25A	0.427405	0.231831	1.287754	0.089*
H25B	0.288428	0.239267	1.284112	0.089*
H25C	0.344034	0.354353	1.262553	0.089*
C26	0.4870 (3)	0.11863 (19)	1.0969 (2)	0.0696 (8)
H26A	0.531384	0.106980	1.012853	0.104*
H26B	0.417007	0.076126	1.129019	0.104*
H26C	0.548252	0.089904	1.136474	0.104*
N1	0.53647 (16)	0.32090 (13)	1.05523 (13)	0.0355 (4)
H1	0.586543	0.281928	0.979462	0.043*
N2	0.66916 (15)	0.50414 (14)	1.02357 (14)	0.0375 (4)
H2	0.642911	0.537491	1.101240	0.045*
Ni1	0.500000	0.500000	1.000000	0.02938 (12)
O1	0.60550 (13)	0.44807 (11)	0.81410 (11)	0.0375 (3)
O2	0.68410 (17)	0.25269 (12)	0.80202 (12)	0.0556 (4)
O3	0.97139 (19)	0.11060 (14)	0.39189 (14)	0.0655 (5)
H3	1.022357	0.063719	0.341249	0.098*
O4	0.93735 (19)	0.21180 (14)	0.23488 (13)	0.0667 (5)
O5	0.65296 (17)	0.61709 (13)	0.28578 (12)	0.0514 (4)
H5A	0.614099	0.681868	0.268228	0.077*
O6	0.56134 (18)	0.68777 (13)	0.46685 (14)	0.0586 (5)
O1W	0.52530 (18)	0.82204 (14)	0.23510 (14)	0.0572 (4)
H1WA	0.497 (2)	0.864 (2)	0.2961 (16)	0.069*
H1WB	0.4581 (17)	0.817 (2)	0.220 (2)	0.069*
O2W	0.1396 (2)	0.96551 (16)	0.22827 (15)	0.0766 (6)
H2WA	0.136 (3)	0.982 (2)	0.1578 (14)	0.092*
H2WB	0.193 (2)	0.8964 (14)	0.223 (2)	0.092*
C10	0.3485 (2)	−0.04332 (18)	0.53520 (18)	0.0441 (5)
C11	0.1006 (2)	0.10963 (18)	0.94265 (18)	0.0444 (5)
C12	0.05830 (19)	0.35574 (17)	0.58011 (17)	0.0381 (4)
C13	0.2524 (2)	0.05118 (17)	0.61571 (17)	0.0385 (4)
C14	0.2198 (2)	0.03788 (17)	0.73836 (17)	0.0408 (5)
H14	0.256160	−0.031537	0.771998	0.049*
C15	0.1326 (2)	0.12821 (17)	0.81121 (16)	0.0374 (4)
C16	0.07906 (19)	0.23208 (17)	0.76055 (17)	0.0378 (4)
H16	0.021331	0.292916	0.808991	0.045*
C17	0.11176 (19)	0.24515 (16)	0.63752 (16)	0.0358 (4)
C18	0.1982 (2)	0.15438 (17)	0.56546 (17)	0.0394 (5)
H18	0.219675	0.162867	0.483182	0.047*
O7	0.3891 (2)	−0.03012 (15)	0.42746 (14)	0.0719 (6)
O8	0.38297 (18)	−0.14101 (13)	0.59355 (13)	0.0612 (5)
H8	0.437129	−0.189255	0.545831	0.092*
O9	0.14899 (19)	0.02202 (15)	0.98884 (13)	0.0682 (5)
O10	0.01397 (18)	0.19926 (14)	1.00279 (13)	0.0635 (5)
H10	−0.003650	0.184057	1.074601	0.095*
O11	−0.01802 (17)	0.43939 (13)	0.65136 (13)	0.0554 (4)
H11	−0.040820	0.497604	0.612177	0.083*
O12	0.08764 (16)	0.36566 (13)	0.47047 (13)	0.0543 (4)

2 Experimental details

The structure was solved using Direct Methods, which yielded the positions of all non-hydrogen atoms. 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 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 atons were set to $1.2U_{eq}$(C, N).

3 Comment

Similar structures to the title compound have been reported [5, 6], which showed two-dimensional sheets constructed by connections of hydrogen bonds. X-ray crystal structural analysis dispalys that the asymmetric unit of the title structure contains one [NiL(BTC)$_2$], one uncoordinated BTC and two free water molecules. The central Ni(II) ion shows a six-coordinated octahedral coordination geometry by coordination with four nitrogen atoms from macrocyclic ligand L in the equatorial plan, and two oxygen atoms from two coordinated BTC in axial positions (see the figure).

The [NiL(BTC)$_2$], uncoordinated BTC and lattice water molecules are linked by O–H···O hydrogen bonds into a two-dimensional sheet. The sheets are further connected via O–H···O hydrogen bonding interactions, generating a three-dimensional structure.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This work was financially supported by the construct program of applied characteristic discipline in the National Science Foundation of Hunan Province (2020JJ9026).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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