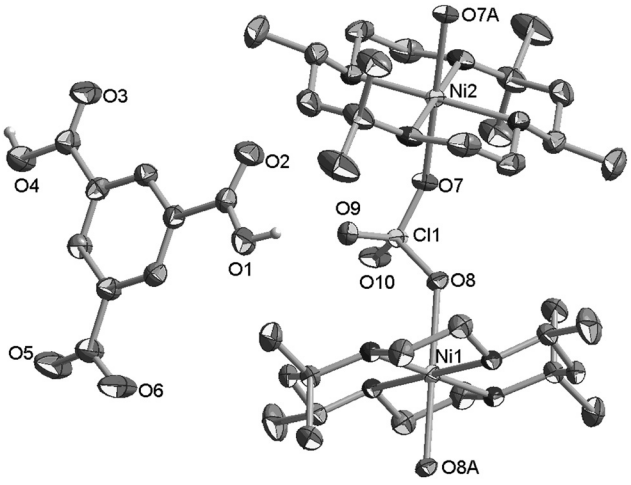
Qiong Wang and Guang-Chuan Ou*

Crystal structure of *catena*-poly[(5,5,7,12,12, 14-hexamethyl -1,4,8,11-tetraazacyclotetradecane-κ^4N,N',N'',N''')nickel(II)-(μ_2-perchlorato-$\kappa^2O:O'$)] 3,5-dicarboxybenzoate – methanol (1/2), $C_{27}H_{49}ClN_4NiO_{12}$



https://doi.org/10.1515/ncrs-2022-0206
Received April 22, 2022; accepted May 30, 2022;
published online June 10, 2022

Abstract

$C_{27}H_{49}ClN_4NiO_{12}$, triclinic, $P\bar{1}$ (no. 2), a = 11.180(2) Å, b = 12.320(3) Å, c = 12.754(3) Å, α = 98.263(2)°, β = 97.524(2)°, γ = 99.470(2)°, V = 1693.1(6) Å^3, Z = 2, $R_{gt}(F)$ = 0.0423, w$R_{ref}(F^2)$ = 0.1238, T = 296(2) K.

CCDC no.: 1903262

The molecular structure is shown in the figure (methanol molecules are omitted for clarity). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Guang-Chuan Ou,** Department of Biology and Chemistry, Hunan University of Science and Engineering, Yongzhou, Hunan, 425199, P. R. China, E-mail: ogcouguangchuan@163.com. https://orcid.org/0000-0002-1005-8519
Qiong Wang, Department of Biology and Chemistry, Hunan University of Science and Engineering, Yongzhou, Hunan, 425199, P. R. China

Table 1: Data collection and handling.

Crystal:	Pink prism
Size:	0.45 × 0.23 × 0.20 mm
Wavelength:	MoKα radiation (0.71073 Å)
μ:	0.72 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}:	19175, 7498, 0.044
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6179
$N(param)_{refined}$:	425
Programs:	Bruker [1], SHELX [2, 3], Diamond [4]

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 trimesic acid (0.210 g, 1 mmol). Crystals of the title compound were obtained by slow evaporation within two weeks.

Experimental details

The structure was solved using direct methods. 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 full-matrix least-squares 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

The design and synthesis of extended bridged polymetallic complexes have a subject of great interest in the development

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

Atom	x	y	z	U_{iso}*/U_{eq}
Ni1	0.000000	1.000000	1.000000	0.02291 (11)
Ni2	0.000000	1.000000	0.500000	0.02367 (11)
Cl1	−0.07274 (5)	0.91024 (4)	0.73258 (4)	0.02700 (13)
O1	−0.39697 (17)	0.83073 (17)	0.69307 (14)	0.0514 (5)
H1A	−0.331490	0.870952	0.690843	0.077*
O2	−0.38133 (19)	0.76220 (17)	0.52536 (15)	0.0535 (5)
O3	−0.70968 (19)	0.44339 (16)	0.33281 (14)	0.0518 (5)
O4	−0.84041 (18)	0.35860 (15)	0.42615 (14)	0.0483 (5)
H4A	−0.862574	0.314966	0.369343	0.072*
O5	−0.7749 (2)	0.45750 (19)	0.82119 (17)	0.0690 (7)
O6	−0.6487 (2)	0.61499 (19)	0.89786 (15)	0.0649 (6)
O7	−0.01320 (14)	0.91526 (13)	0.63719 (11)	0.0308 (3)
O8	0.01223 (13)	0.97156 (13)	0.82833 (11)	0.0303 (3)
O9	−0.18267 (13)	0.96314 (14)	0.72100 (12)	0.0333 (4)
O10	−0.10918 (17)	0.79321 (13)	0.74527 (12)	0.0396 (4)
O11	−0.1388 (3)	0.5641 (2)	0.8576 (2)	0.0780 (7)
H11	−0.190 (4)	0.580 (3)	0.795 (4)	0.094*
O12	0.6896 (3)	1.4120 (2)	0.9130 (2)	0.0799 (8)
H12	0.736 (4)	1.457 (4)	0.903 (4)	0.096*
N1	0.14116 (16)	0.91491 (15)	1.04159 (14)	0.0270 (4)
H1	0.154635	0.929888	1.120221	0.032*
N2	0.11609 (16)	1.15188 (15)	1.00967 (14)	0.0273 (4)
H2	0.133042	1.187352	1.085272	0.033*
N3	0.06524 (18)	0.86930 (15)	0.41673 (15)	0.0327 (4)
H3	0.084997	0.897337	0.351731	0.039*
N4	0.17403 (17)	1.08392 (17)	0.57273 (14)	0.0337 (4)
H4	0.210524	1.125235	0.520953	0.040*
C1	−0.4296 (2)	0.7573 (2)	0.60398 (19)	0.0355 (5)
C2	−0.7465 (2)	0.43370 (19)	0.41684 (19)	0.0352 (5)
C3	−0.7029 (3)	0.5388 (2)	0.8146 (2)	0.0441 (6)
C4	−0.5340 (2)	0.66664 (19)	0.60971 (18)	0.0324 (5)
C5	−0.5904 (2)	0.59457 (19)	0.51665 (18)	0.0317 (5)
H5	−0.563774	0.603960	0.451868	0.038*
C6	−0.6866 (2)	0.50810 (19)	0.51923 (18)	0.0325 (5)
C7	−0.7230 (2)	0.4921 (2)	0.61662 (19)	0.0363 (5)
H7	−0.786728	0.433907	0.618842	0.044*
C8	−0.6649 (2)	0.5624 (2)	0.71076 (19)	0.0356 (5)
C9	−0.5717 (2)	0.6509 (2)	0.70739 (19)	0.0359 (5)
H9	−0.534562	0.699644	0.770075	0.043*
C10	0.0842 (2)	0.79573 (19)	1.0155 (2)	0.0362 (5)
H10A	0.134913	0.752295	1.053213	0.043*
H10B	0.077087	0.769749	0.939050	0.043*
C11	0.2679 (2)	0.9451 (2)	1.01443 (18)	0.0320 (5)
C12	0.2722 (2)	0.9001 (2)	0.8968 (2)	0.0436 (6)
H12A	0.260537	0.820087	0.886252	0.065*
H12B	0.350552	0.929700	0.879052	0.065*
H12C	0.208305	0.922274	0.851457	0.065*
C13	0.3587 (2)	0.8975 (3)	1.0880 (2)	0.0474 (6)
H13A	0.354114	0.924303	1.161584	0.071*
H13B	0.440536	0.920986	1.074248	0.071*
H13C	0.338069	0.817446	1.074114	0.071*
C14	0.3049 (2)	1.0736 (2)	1.03913 (18)	0.0342 (5)
H14A	0.298744	1.096684	1.113919	0.041*
H14B	0.390973	1.092277	1.032502	0.041*
C15	0.2365 (2)	1.1460 (2)	0.97418 (18)	0.0332 (5)
H15	0.221561	1.111140	0.898438	0.040*
C16	0.3166 (3)	1.2614 (3)	0.9853 (3)	0.0588 (8)
H16A	0.277394	1.304433	0.938941	0.088*
H16B	0.395155	1.253551	0.965611	0.088*
H16C	0.327715	1.298728	1.058284	0.088*
C17	0.0418 (2)	1.21914 (19)	0.95121 (19)	0.0342 (5)
H17A	0.034646	1.194868	0.874480	0.041*
H17B	0.080973	1.297238	0.968099	0.041*
C18	0.1515 (3)	1.1665 (2)	0.66131 (19)	0.0442 (6)
H18A	0.224266	1.223969	0.685418	0.053*
H18B	0.133824	1.129747	0.721401	0.053*
C19	0.2584 (2)	1.0093 (2)	0.6068 (2)	0.0441 (6)
H19	0.218750	0.962894	0.653380	0.053*
C20	0.3822 (3)	1.0748 (4)	0.6699 (3)	0.0745 (11)
H20A	0.428257	1.111673	0.622485	0.112*
H20B	0.427762	1.024120	0.700366	0.112*
H20C	0.367872	1.129300	0.726357	0.112*
C21	0.2785 (2)	0.9327 (3)	0.5086 (2)	0.0501 (7)
H21A	0.354344	0.906492	0.527527	0.060*
H21B	0.291588	0.977858	0.453237	0.060*
C22	0.1793 (3)	0.8300 (2)	0.4582 (2)	0.0459 (6)
C23	0.1539 (3)	0.7524 (3)	0.5402 (2)	0.0562 (8)
H23A	0.109834	0.786088	0.591767	0.084*
H23B	0.230392	0.740500	0.576339	0.084*
H23C	0.105739	0.682089	0.503756	0.084*
C24	0.2271 (4)	0.7669 (3)	0.3632 (3)	0.0731 (11)
H24A	0.167984	0.700781	0.331396	0.110*
H24B	0.303526	0.746396	0.388673	0.110*
H24C	0.239344	0.814240	0.310480	0.110*
C25	−0.0451 (3)	0.7815 (2)	0.3767 (2)	0.0456 (6)
H25A	−0.064876	0.740593	0.433599	0.055*
H25B	−0.028919	0.729355	0.318003	0.055*
C26	−0.0301 (4)	0.5299 (4)	0.8309 (4)	0.1033 (15)
H26A	0.001811	0.572997	0.780358	0.155*
H26B	−0.048258	0.452191	0.799743	0.155*
H26C	0.029788	0.541328	0.894612	0.155*
C27	0.5846 (4)	1.4032 (4)	0.8396 (4)	0.0979 (15)
H27A	0.527166	1.441121	0.872760	0.147*
H27B	0.548357	1.325915	0.815819	0.147*
H27C	0.605226	1.436612	0.779215	0.147*

of materials chemistry. Many extended bridged complexes such as μ-tetrahedron, μ-succinate, have been synthesized [5–7].

X-ray crystal structural analysis reveals that the asymmetric unit of the title structure contains one $[NiL]^{2+}$ (two halfs on centers of symmetry), one $[ClO_4]^-$ and one $[C_9H_5O_6]^-$ plus two methanol molecules. Each Ni(II) atom displays a six-coordinate octahedral coordination

geometry by coordination with four nitrogen atoms of ligand L in the equatorial plan, and two oxygen atoms of $[ClO_4]^-$ in axial positions. Each $[ClO_4]^-$ anion bridges two adjacent $[NiL]^{2+}$ cations, forming a one-dimensional chain. The chains are further connected *via* O–H···O hydrogen-bonding interactions, generating a two-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 scientific research fund of Hunan provincial education department (19A068) and the construct program of applied characteristic discipline in Hunan University of Science and Engineering.

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

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