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The crystal structure of *catena-poly*(μ_2 -4,4'-bipyridine- $\kappa^2N:N'$)-tetrakis(μ_2 -2-((3,5,6-trichloropyridin-2-yl)oxy)acetato- $\kappa^2O:O'$)dinickel(II)], $C_{19}H_{10}Cl_6N_3NiO_6$

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Abstract

$C_{19}H_{10}Cl_6N_3NiO_6$, tetragonal, $I\bar{4}$ (no. 82), $a = 13.1205(4)$ Å, $c = 14.2717(6)$ Å, $V = 2456.84(18)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0384$, $wR_{ref}(F^2) = 0.0756$, $T = 293.2(3)$ K.

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A part of the molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

$NiCl_2 \cdot 6H_2O$ (0.2 mmol, 0.050 g) and 2-((3,5,6-trichloropyridin-2-yl)oxy)acetic acid (HL, 0.2 mmol, 0.051 g), 4,4'-bipyridine (bipy, 0.2 mmol, 0.040 g) were dissolved in

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Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.25 × 0.22 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.48 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
θ_{max} , completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	2889, 2262, 0.016
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2029
$N(param)_{refined}$:	168
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
C1	0.6268(4)	0.7156(4)	0.3399(5)	0.0486(14)
C2	0.5895(5)	0.7343(5)	0.4284(5)	0.0538(17)
C3	0.6500(5)	0.7887(5)	0.4894(5)	0.0612(18)
H3	0.6266	0.8041	0.5493	0.073*
C4	0.7450(5)	0.8201(5)	0.4612(4)	0.0519(16)
C5	0.7762(4)	0.7962(4)	0.3705(4)	0.0400(14)
C6	0.9045(4)	0.7915(4)	0.2551(5)	0.0410(12)
H6A	0.963(4)	0.837(4)	0.240(4)	0.058(16)*
H6B	0.852(4)	0.803(4)	0.203(4)	0.041(16)*
C7	0.9370(3)	0.6806(3)	0.2588(4)	0.0307(10)
C8	0.9605(5)	0.5758(4)	0.5498(4)	0.0495(16)
H8	0.9322	0.6302	0.5173	0.059*
C9	0.9587(5)	0.5788(4)	0.6471(4)	0.0554(17)
H9	0.9295	0.6341	0.6779	0.066*
C10	1.0000	0.5000	0.6979(4)	0.0372(15)
Cl1	0.55257(12)	0.65150(14)	0.25815(16)	0.0784(5)
Cl2	0.47101(15)	0.69336(17)	0.46484(17)	0.0968(7)
Cl3	0.82264(18)	0.8895(2)	0.53337(15)	0.1084(9)
N1	0.7181(3)	0.7445(3)	0.3116(3)	0.0414(11)
N2	1.0000	0.5000	0.5007(3)	0.0312(11)
Ni1	1.0000	0.5000	0.34666(5)	0.0241(2)
O1	0.8688(3)	0.8284(3)	0.3434(3)	0.0446(9)
O2	0.9499(3)	0.6397(3)	0.3377(3)	0.0392(9)
O3	0.9518(3)	0.6411(3)	0.1800(2)	0.0374(9)

20 mL H₂O and then the pH of the obtained mixture was neutralized with KOH (0.5 mol · L⁻¹) to pH = 7.0. After that, the mixed solution was sealed in a 25 mL Teflon reactor and kept under autogeneous pressure at 393 K for 3 days. After cooling

to room temperature at a rate of 279 K · h^{−1}, green block crystals of the title compound were obtained. Yield: 10 mg (8%, based on Ni). Anal. Calcd. for C₁₉H₁₀Cl₆N₃NiO₆ (%): C, 35.21; H, 1.54; N, 6.49. Found: C, 35.28; H, 1.61; N, 6.42.

Experimental details

Empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK. Using Olex2 [2], the structure was solved with the ShelXT [3] and refined with the ShelXL [4] refinement package.

The H atoms bonded to C atoms were fixed, with C—H distance of 0.93 Å; and/or positioned geometrically in the riding-model approximation, with C—H distance of 0.97 Å; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Comment

At the beginning of the coordination chemistry, aromatic carboxylate ligands have been adopted as linkers to build metal-organic frameworks with interesting topologies and potential applications [5]. Recently, modification of aromatic carboxylate by various substituent groups on the aromatic ring such as MeO[−] [6], ^tBu[−] [7], −OH, −SO₃H [8–10], −F [11], −Cl [12], −NH₂ [13] has been employed. Due to the steric and/or electronic effects of the substituents, these modified ligands may afford new assemblies. One example of three chloro substitute aromatic carboxylic ligand is 2-((3,5,6-trichloropyridin-2-yl)oxy)acetic acid (HL).

HL contains one flexible CH₂- group. Therefore, the carboxy group can twist freely to meet the requirement of coordination geometry of metal center in the assembly process. Therefore, HL is an excellent candidate for the construction of new complexes.

Single-crystal X-ray diffraction analysis shows that the title structure consists of a chain structure in which the asymmetric unit is comprised of one half of a Ni^{II} ion, one complete L[−] ligand and one quarter of a bipy ligand.

Two Ni^{II} ions are bridged by four equivalent μ₂-coordinated L[−] with their oxygen atoms and afford a dimer [Ni₂L₄] species, with the Ni1 ··· Ni1A distance of 2.759 Å (symmetry codes: (A) 3/2 − x, 1/2 + y, 1/2 − z). The dimer moieties are connected by bipy to form the 1D polymer along the c axis finally (see the figure; only the asymmetric unit is labelled).

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