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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- $\kappa^2O:O'$)dicobalt(II)], $C_{19}H_{10}Cl_6CoN_3O_6$

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Abstract

$C_{19}H_{10}Cl_6CoN_3O_6$, tetragonal, $I\bar{4}$ (no. 82), $a = 13.1152(4)$ Å, $c = 14.2497(6)$ Å, $V = 2451.07(18)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0359$, $wR_{ref}(F^2) = 0.0843$, $T = 293.2(3)$ K.

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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.

Table 1: Data collection and handling.

Crystal:	Blue block
Size:	$0.27 \times 0.24 \times 0.20$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.40 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
θ_{max} , completeness:	25.5° , $>99\%$
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	2720, 1844, 0.018
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1710
$N(param)_{refined}$:	160
Programs:	SHELX [1], CrysAlis ^{PRO} [2]

Source of material

$CoCl_2 \cdot 6H_2O$ (0.2 mmol, 0.048 g) and 2-((3,5,6-trichloropyridin-2-yl)oxy)acetic acid (Htcpa, 0.2 mmol, 0.052 g), 4,4'-bipyridine (bipy, 0.2 mmol, 0.039 g) were dissolved in 20 mL H_2O and then the pH of the obtained mixture was adjusted with KOH (0.5 mol·L⁻¹) to pH = 6.5. After that, the mixed solution was sealed in a 25 mL Teflon reactor and kept under autogeneous pressure at 393 K for 4 days. After cooling to room temperature at a rate of 279 K·h⁻¹, red block shaped crystals of the title compound were obtained. Yield: 16 mg (12%, based on Co). Anal. Calcd. for $C_{19}H_{10}Cl_6CoN_3O_6$ (%): C, 35.19; H, 1.54; N, 6.48. Found: C, 35.25; H, 1.48; N, 6.41.

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

Atom	x	y	z	U_{iso}^*/U_{eq}
Co1	0.5000	0.0000	0.65336(5)	0.0227(2)
Cl1	0.65160(15)	0.44725(13)	0.74168(17)	0.0810(6)
Cl2	0.69339(19)	0.52911(17)	0.53514(19)	0.1002(8)
Cl3	0.8892(2)	0.1772(2)	0.46649(16)	0.1107(9)
O1	0.8284(3)	0.1313(3)	0.6567(3)	0.0463(10)
O2	0.6397(3)	0.0498(3)	0.6623(3)	0.0423(9)
O3	0.6414(3)	0.0479(3)	0.8200(2)	0.0416(10)
N1	0.7449(4)	0.2823(4)	0.6883(3)	0.0422(12)
N2	0.5000	0.0000	0.4994(3)	0.0346(12)
C1	0.7158(5)	0.3736(5)	0.6601(5)	0.0526(15)
C2	0.7345(5)	0.4103(5)	0.5709(5)	0.0572(18)
C3	0.7882(6)	0.3494(6)	0.5101(5)	0.066(2)
H3	0.8028	0.3720	0.4498	0.080*
C4	0.8201(5)	0.2550(5)	0.5391(5)	0.0548(17)
C5	0.7959(4)	0.2244(5)	0.6300(4)	0.0435(15)
C6	0.7909(4)	0.0955(4)	0.7452(5)	0.0443(12)
H6A	0.7981	0.1492	0.7915	0.053*
H6B	0.8320	0.0381	0.7656	0.053*
C7	0.6806(4)	0.0632(4)	0.7403(4)	0.0337(11)
C8	0.4241(5)	−0.0394(5)	0.4503(4)	0.0500(16)
H8	0.3691	−0.0669	0.4828	0.060*
C9	0.4219(5)	−0.0420(6)	0.3530(4)	0.0565(17)
H9	0.3672	−0.0724	0.3223	0.068*
C10	0.5000	0.0000	0.3016(4)	0.0401(15)

Experimental details

H atoms were positioned geometrically in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Comment

At the initial stage of coordination chemistry, aromatic carboxylate ligands have been selected as linkers to construct metal-organic frameworks with intriguing topologies and potential applications [3]. Especially paddle wheel nodes are of significant interest [4]. Recently, modification of aromatic carboxylate by various substituent groups on the aromatic ring such as −OH, −SO₃H [5, 6], −F [7], −Cl [8], −Br [9], −NH₂ [10] has been employed. Due to the steric and/or electronic effects of the substituent groups, these modified ligands may afford new supramolecular assemblies because of their special linking types and ligand-metal interactions.

One example of three chloro substitute aromatic carboxylate is Htcpa. It is well known that Htcpa is commonly used as herbicide in agriculture, but its complexes have not been reported so far. Recently, we have published its complexes of 1D Ni(II) [11] and binuclear Cd(II) [12]. In this paper, we describe 1D Co(II) compound containing Htcpa.

Single-crystal X-ray diffraction analysis reveals that title compound shows a 1D linear chain structure in which the

asymmetric unit contains one half of a Co^{II} ion, one tcpa[−] ligand and one quarter of a bipy molecule. Co^{II} ions are pairwise bridged by four equivalent μ_2 coordinated tcpa[−] to give the paddle wheel node [Co₂(tcpa)₄], with the Co1⋯Co1A distance of 2.754 Å (symmetry codes: (A) $1/2 + y$, $1/2 - x$, $3/2 - z$) (the figure). The dinuclear units are connected by bipy ligands to form chains along the *c* axis.

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