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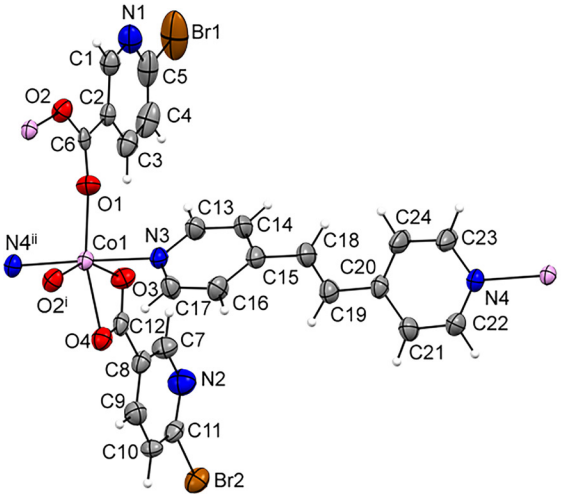
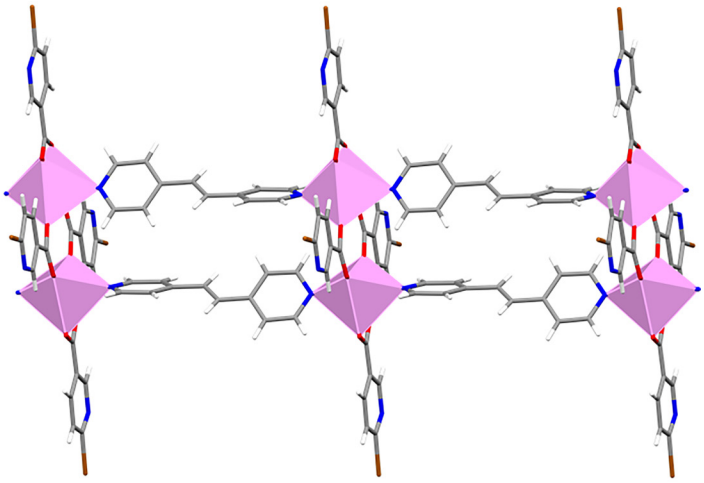
The double polymeric chain of *catena*-poly[(μ_2-6-bromopyridine-3-carboxylato-κ^2O,O')(6-bromopyridine-3-carboxylato-κ^2O,O')(μ_2-1,2-bis(4-pyridyl)ethylene-$\kappa^2N:N'$)cobalt(II)], $C_{24}H_{16}CoBr_2N_4O_4$





https://doi.org/10.1515/ncrs-2022-0460
Received September 19, 2022; accepted October 10, 2022; published online October 24, 2022

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Table 1: Data collection and handling.

Crystal:	Prism, pink
Size:	0.09 × 0.05 × 0.04 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	4.13 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω-scans
θ_{max}, completeness:	33.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	32,374, 8150, 0.058
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 5169
$N(param)_{refined}$:	317
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], MERCURY [4]

Abstract

$C_{24}H_{16}CoBr_2N_4O_4$, monoclinic, $P2_1/c$ (no. 14), a = 11.1134(4) Å, b = 16.1731(6) Å, c = 13.7057(5) Å, β = 105.363(4)°, V = 2375.41(16) Å^3, Z = 4, $R_{gt}(F)$ = 0.0588, $wR_{ref}(F^2)$ = 0.1101, T = 170(2) K.

CCDC no.: 2211994

The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.16732 (3)	0.42379 (2)	0.05212 (3)	0.02422 (10)
Br1	0.50460 (5)	0.88395 (4)	0.09718 (4)	0.0987 (2)
Br2	0.89474 (3)	0.20186 (2)	0.23329 (3)	0.04373 (11)
N1	0.2630 (3)	0.82589 (19)	0.0492 (2)	0.0503 (8)
N2[a]	0.7286 (3)	0.3350 (2)	0.1967 (2)	0.0437 (7)
C10A[a]	0.7286 (3)	0.3350 (2)	0.1967 (2)	0.0437 (7)
H10A[a]	0.802165	0.367757	0.214353	0.052*
N3	0.1675 (2)	0.43226 (15)	0.20922 (17)	0.0308 (5)
N4	0.1756 (2)	0.41281 (15)	0.89617 (17)	0.0313 (5)
O1	0.1325 (2)	0.54574 (13)	0.03763 (17)	0.0430 (5)
O2	−0.00734 (18)	0.64423 (13)	−0.01935 (15)	0.0344 (5)
O3	0.37004 (19)	0.43728 (13)	0.10074 (17)	0.0389 (5)
O4	0.28492 (19)	0.31456 (13)	0.09376 (16)	0.0356 (5)
C1	0.1758 (3)	0.7660 (2)	0.0312 (2)	0.0368 (7)
H1	0.090540	0.781934	0.011106	0.044*
C2	0.2037 (3)	0.68259 (18)	0.0403 (2)	0.0279 (6)
C3	0.3278 (3)	0.6595 (2)	0.0694 (2)	0.0412 (8)
H3	0.350199	0.602738	0.077083	0.049*
C4	0.4185 (3)	0.7196 (3)	0.0872 (3)	0.0540 (10)
H4	0.504596	0.705526	0.106796	0.065*
C5	0.3807 (4)	0.7998 (3)	0.0758 (3)	0.0544 (11)
C6	0.1015 (3)	0.61920 (17)	0.01812 (19)	0.0257 (6)
C7	0.6131 (3)	0.3699 (2)	0.1695 (3)	0.0421 (8)
H7	0.605662	0.428453	0.167706	0.050*
C8	0.5064 (3)	0.3219 (2)	0.1443 (2)	0.0334 (7)
C9	0.5214 (3)	0.2371 (2)	0.1477 (3)	0.0403 (7)
H9	0.449249	0.202936	0.131095	0.048*
C10[a]	0.6356 (3)	0.20084 (18)	0.1741 (2)	0.0377 (7)
H10[a]	0.645151	0.142446	0.175798	0.045*
N2A[a]	0.6356 (3)	0.20084 (18)	0.1741 (2)	0.0377 (7)
C11	0.7334 (3)	0.2514 (2)	0.1975 (2)	0.0340 (7)
C12	0.3801 (3)	0.3605 (2)	0.1114 (2)	0.0314 (6)
C13	0.2208 (3)	0.4954 (2)	0.2668 (2)	0.0401 (8)
H13	0.257064	0.538129	0.236420	0.048*
C14	0.2262 (3)	0.5022 (2)	0.3679 (2)	0.0429 (8)
H14	0.264025	0.549233	0.405092	0.051*
C15	0.1766 (3)	0.4406 (2)	0.4152 (2)	0.0369 (7)
C16	0.1220 (3)	0.3740 (2)	0.3554 (2)	0.0402 (8)
H16	0.086848	0.329652	0.384129	0.048*
C17	0.1191 (3)	0.3727 (2)	0.2544 (2)	0.0372 (7)
H17	0.080553	0.326998	0.214716	0.045*
C18	0.1799 (3)	0.4481 (2)	0.5229 (2)	0.0439 (8)
H18	0.184282	0.502430	0.549961	0.053*
C19	0.1774 (3)	0.3863 (2)	0.5856 (2)	0.0392 (7)
H19	0.174347	0.331542	0.559872	0.047*
C20	0.1792 (3)	0.39696 (19)	0.6921 (2)	0.0326 (7)
C21	0.2222 (3)	0.3346 (2)	0.7624 (2)	0.0402 (8)
H21	0.254078	0.284831	0.742227	0.048*
C22	0.2186 (3)	0.3448 (2)	0.8612 (2)	0.0413 (8)
H22	0.248515	0.300953	0.907345	0.050*
C23	0.1321 (4)	0.4716 (2)	0.8285 (2)	0.0497 (9)
H23	0.099111	0.520273	0.850384	0.060*
C24	0.1322 (4)	0.4661 (2)	0.7279 (2)	0.0543 (10)
H24	0.099535	0.510271	0.683062	0.065*

[a]Occupancy: 0.5.

atoms including atomic coordinates and displacement parameters.

Source of material

6-Bromonicotinic acid (0.1005 g, 0.4975 mmol) was dissolved in 2 mL of DMF, 1,2-bis(4-pyridyl)ethylene (0.0454 g, 0.2491 mmol) was dissolved in 2 mL of DMF and cobalt(II) nitrate hexahydrate (0.0699 g, 0.2402 mmol) was dissolved in 2 mL of DMF. The solutions of the two ligands were first mixed together under stirring. The resulting solution was then slowly added to the cobalt(II) nitrate solution under stirring. The obtained reaction mixture was left to slowly evaporate at room temperature and atmospheric pressure for 25 days. The obtained colorless crystals were filtered off and the remaining pink mother liquor was again left to slowly evaporate for another 13 days. This time, pink crystals of the target compound were obtained concomitantly with colorless crystals. The mixed crystals were filtered off, dried in air and the colorless crystals were removed manually. Yield: 0.0042 g (3%).

Experimental details

The positions of hydrogen atoms belonging to the Csp^2 carbon atoms were geometrically optimized applying the riding model (Csp^2–H, 0.95 Å, U_{iso}(H) = 1.2U_{eq}(C)). The N2 and C10 atoms are substitutionally disordered and the EADP and EXYZ instructions were used during refinement, while the site occupancy factors for N2, C10 and H10 atoms were set to 0.5.

Comment

A design of coordination polymers has become an important field of crystal engineering in the recent years due to their various functional properties and many possible applications e.g. in catalysis, gas and energy storage, gas separation, magnetism, luminescence, molecular sensing, biomedical imaging [5–9]. Cobalt(II) and nickel(II) coordination polymers with halogeno-substituted pyridine-3-carboxylates (nicotinates e.g. 2-chloronicotinate [10], 6-chloronicotinate [11], 6-fluoronicotinate [12], 5-bromonicotinate [10]) and bipyridine derivatives (e.g. 4,4′-bipyridine) have recently started to attract more interest. Still, only a limited number of these compounds have been described in the literature so far, all containing the bridging 4,4′-bipyridine ligand [10–12]. We wanted to enhance further the structural

diversity of this type of coordination polymers by replacing the 4,4′-bipyridine with a related bipyridine-derived ligand e.g. bis(4-pyridyl)ethylene, (1,2-bpe). Additionally, the coordinating properties of 6-bromonicotinate still remain unexplored, as it has never been used in the design and assembly of coordination polymers [13]. Hence, we have prepared a new 1-D cobalt(II) coordination polymer with 6-bromonicotinate (6-Brnic) and 1,2-bis(4-pyridyl)ethylene by a reaction of cobalt(II) nitrate hexahydrate, 6-bromonicotinic acid and 1,2-bis(4-pyridyl)ethylene (molar ratio 1:2:1) in DMF solution at room temperature and atmospheric pressure.

The asymmetric unit is composed of a cobalt(II) ion, two 6-bromonicotinate ligands and a single 1,2-bis(4-pyridyl) ethylene ligand. The cobalt(II) ion is octahedrally coordinated by carboxylate O3 and O4 atoms (from an *O*,*O*′-chelating 6-bromonicotinate ligand) and by carboxylate O1 and O2^{i} atoms (from two separate *O*,*O*′-bridging 6-bromonicotinate ligands) in the equatorial plane, whilst pyridine N3 and N4^{ii} atoms (from two separate *N*:*N*′-bridging 1,2-bis(4-pyridyl) ethylene ligands) are placed in the axial positions (the bond angle N3–Co1–N4^{ii} = 177.37(9)°, symmetry codes (i): $-x$, $-y+1$, $-z$; (ii): x, y, $z-1$). The cobalt(II) ions are alternately connected by *N*:*N*′-bridging 1,2-bis(4-pyridyl)ethylene ligands along the [001] direction, whilst the adjacent cobalt(II) ions are also joined along the [010] direction by a pair of *O*,*O*′-bridging 6-bromonicotinate ligands, giving rise to an infinite double 1-D polymeric chain running in the [001] direction. There are two types of centrosymmetric rings formed within this double chain: an 8-membered ring formed in between two cobalt(II) ions and two *O*,*O*′-bridging 6-bromonicotinate ligands, and a macrocyclic 30-membered ring formed in between four cobalt(II) ions, two *O*,*O*′-bridging 6-bromonicotinate ligands and two *N*:*N*′-bridging 1,2-bis(4-pyridyl)ethylene ligands. The aforementioned double chains are assembled into a 3-D architecture by weak interactions only, in particular π–π interactions between 6-bromonicotinate pyridine rings. A nickel(II) polymer with 6-fluoronicotinate and 4,4′-bipyridine [12] and a cobalt(II) polymer with 2-chloronicotinate and 4,4′-bipyridine [10] are structurally the most similar compounds. Both of these coordination polymers display only single 1-D polymeric chains, as opposed to the double 1-D chains of the title compound. This difference is due to the presence of only a single type of bridging ligands (4,4′-bipyridine) in the mentioned coordination polymers [10, 12], in comparison with two types of bridging ligands (*O*,*O*′-6-Brnic and *N*:*N*′-1,2-bpe) in the title compound. Consequently, the mentioned coordination polymers contain *O*-monodentate halonicotinate ligands (6-fluoronicotinate [12] or 2-chloronicotinate [10]) and coordinated water molecules, whilst the title compound contains bidentate *O*,*O*′-chelating 6-bromonicotinate ligands and no water molecules.

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

Research funding: This research and the open access paper charge were funded by the Faculty of Chemistry and Technology, University of Split institutional funding.

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

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