Crystal structure of *catena*-[dichlorido-μ_2-4,4'-dithiodipyridine-κ^2N:N'-zinc(II)], $C_{10}H_8Cl_2N_2S_2Zn$

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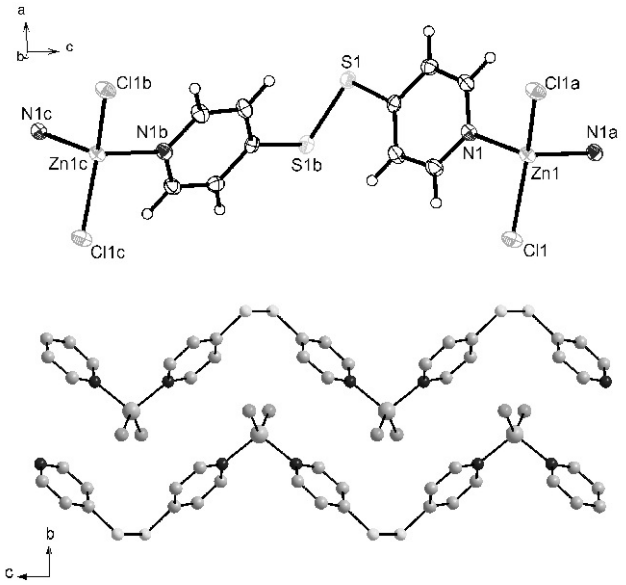

Abstract

$C_{10}H_8Cl_2N_2S_2Zn$, monoclinic, *C*2/*c* (no. 15), a = 12.317(2) Å, b = 9.868(2) Å, c = 10.947(2) Å, β = 92.37(2)°, V = 1329.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.132, T = 110 K.

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.13×0.25×0.27 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	25.39 cm^{-1}
Diffractometer, scan mode:	Xcalibur^{TM}2, Oxford Diffraction, ω
$2\theta_{max}$:	56.8°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2799, 2799
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2444
$N(param)_{refined}$:	79
Programs:	CrysAlisPro [9], SUPERFLIP [10], EDMA [11], SHELXL-97 [12], DIAMOND [13], enCIFer [14]

Source of material

All starting materials were purchased and used as received. Methanol was of reagent grade. $ZnCl_2$ (7 mg, 0.05 mmol) was dissolved in 2 mL of methanol, $AgCF_3SO_3$ (23 mg, 0.09 mmol) was added and the mixture was stirred for 20 min. in the dark. Subsequently, the precipitate was removed by centrifugation and a solution of 1,10-phenanthroline (9 mg, 0.05 mmol) in 8 mL of methanol was added. The resulting solution was carefully layered onto a solution of 4,4'-dithiopdipyridine (11 mg, 0.05 mmol) in 10 mL of dichloromethane. After standing a couple of days at room temperature, while the solvent was allowed to evaporate slowly, a few colourless crystals of the title compound were found. The presence of chlorido ligands in the title compound can be attributed to incomplete chloride-triflate exchange.

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Experimental details

The crystal studied was a non-merohedral twin. The twin operation is a twofold rotation about the *c** axis. The twinning was taken into account in the data reduction and structure refinement. The crystal structure was solved *ab initio* by charge flipping, using detwinned HKLF 4 data. The final structure refinement was carried out using the HKLF 5 option of SHELXL-97. Refinement of the ratio of the twin components yielded 0.8001(9):0.1991(9). Hydrogen atoms were placed at geometrically calculated positions and refined with constrained C–H distances of 0.95Å and $U_{iso}(H) = 1.2U_{eq}(C)$, allowing them to ride on the parent carbon atoms.

Discussion

Crystal engineering of coordination polymers has attracted considerable interest since the early 1990s. Especially a plethora of one-dimensional coordination polymers have been described [1]. In this contribution, we report on the structure of a one-dimensional coordination polymer of the arched chain type, $[ZnCl_2(\mu\text{-dtdp})]_n$(dtdp = 4,4'-dithiodipyridine), comprising $ZnCl_2$ units joined by the axially chiral bent bridging ligand dtdp [2]. Zn^{2+} is known to be particularly suited to crystal engineering of coordination polymers and has been widely used to this end [3]. The title compound was obtained unintentionally during attempts to *crystal engineer* polymeric or discrete metallosupramolecular compounds from Zn^{2+} as metal nodes and dtdp, under the control of the chelate 1,10-phenanthroline (phen) coligand as a *cis*-protecting group. The attempt to combine $Zn(phen)^{2+}$ building blocks with dtdp was, however, unsuccessful here, similar as already observed in an earlier, recently published work [4]. In contrast, a discrete M_2L_2-metallamacrocycle and a one-dimensional arched chain coordination polymer were previously successfully synthesised, respectively from $Cu(phen)^{2+}$ and $Cd(phen)^{2+}$ building blocks and dtdp [5]. In the title compound, the Zn^{2+} ions adopt a tetrahedral coordination sphere, comprised of two pyridyl groups of the dtdp ligands and two chlorido ligands. In the crystal, twofold crystallographic rotation axes parallel to the *b* axis direction run through both the $ZnCl_2$ unit and the disulfide moiety of the dtdp ligand. Thus, the asymmetric unit comprises only half of each unit. The Zn–N and Zn–Cl bond lengths are 2.047(2) and 2.2133(7) Å, respectively. The N–Zn–N angle is 103.6(1)° and the Cl–Zn–Cl angle is 126.28(4)°. The C–S–S–C torsion angle of dtdp is larger than the idealised 90° with a value of 91.9(2)°. Each polymeric strand contains only dtdp

ligands of the same handedness (*i. e.* either the left-handed *M* or the right-handed *P* form) and are propagated by translational symmetry in the [001] direction, with a repeat unit corresponding to the *c* lattice parameter [10.947(2) Å]. The space group symmetry (*C*2/*c*) generates the enantiomeric conformation. The arched chains are tightly packed in such a way that the $ZnCl_2$ units dovetail into the arch formed by the dtpd ligands of an adjacent polymeric chain in the *b* axis direction. The layers thus formed stack along the *b* axis direction. Two analogous arched chain coordination polymers composed of tetrahedally coordinated Zn^{2+} ions and dtdp, which are isomorphous to the title compound, were reported previously: $[Zn(CH_3COO)_2(\mu\text{-dtdp})]_n$ (CSD refcode: FAYQUS) [6] and $[Zn(NCS)_2(\mu\text{-dtdp})]_n$ (CSD refcode: CEBLUR) [7]. It should be noted that both were originally described in the non-centrosymmetic space group *Cc,* but a re-interpretation of both, where the space group *C*2/*c* was assigned (CSD refcodes: FAYQUS01 and CEBLUR01), was reported afterwards [8].

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	*8f*	0.6572	0.2576	0.1601	0.023
H(3)	*8f*	0.6901	0.0997	0.0064	0.022
H(5)	*8f*	0.3944	0.2062	–0.1375	0.025
H(6)	*8f*	0.3788	0.3581	0.0219	0.025

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	4*e*	½	0.44980(4)	¼	0.0168(2)	0.0164(2)	0.0167(2)	0	–0.0029(2)	0
Cl(1)	8*f*	0.34197(5)	0.55114(6)	0.21146(6)	0.0181(3)	0.0233(4)	0.0279(3)	0.0036(2)	–0.0049(2)	–0.0014(2)
S(1)	8*f*	0.56869(5)	0.01630(7)	–0.19645(5)	0.0215(3)	0.0192(3)	0.0163(3)	0.0029(2)	0.0025(2)	0.0007(2)
N(1)	8*f*	0.5211(2)	0.3214(2)	0.1060(2)	0.019(1)	0.017(1)	0.0171(9)	–0.0005(8)	–0.0013(7)	0.0011(7)
C(2)	8*f*	0.6109(2)	0.2460(3)	0.0991(2)	0.018(1)	0.020(1)	0.018(1)	–0.002(1)	–0.0031(9)	0.0028(9)
C(3)	8*f*	0.6255(2)	0.1524(3)	0.0078(2)	0.017(1)	0.019(1)	0.021(1)	–0.0005(9)	0.0012(9)	0.0025(9)
C(4)	8*f*	0.5439(2)	0.1371(2)	–0.0816(2)	0.021(1)	0.014(1)	0.014(1)	–0.0005(9)	0.0034(8)	0.0028(8)
C(5)	8*f*	0.4513(2)	0.2148(3)	–0.0766(2)	0.024(1)	0.020(1)	0.017(1)	0.002(1)	–0.0040(9)	0.0002(9)
C(6)	8*f*	0.4429(2)	0.3050(3)	0.0183(2)	0.022(1)	0.020(1)	0.021(1)	0.005(1)	–0.0024(9)	0.0000(9)

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