

Qi-Ming Qiu*, Jian-Biao Song, Li Yan, Ai-Guo Dong, Chuan-Tao Li and Zhi-Yuan Zheng*

The crystal structure of 1,2-bis(pyridinium-4-yl)ethane dperchlorate, $C_{12}H_{14}N_2 \cdot 2ClO_4$ – a second polymorph

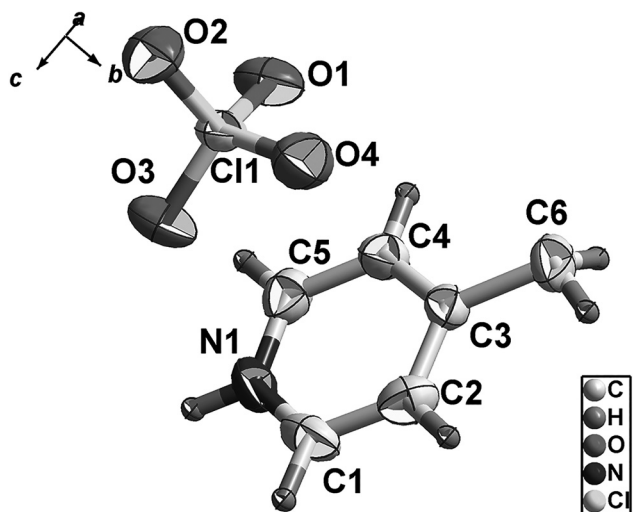


Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.10 × 0.05 × 0.04 mm
Wavelength:	Cu K α radiation (1.54178 Å)
μ :	4.17 mm ⁻¹
Diffractometer, scan mode:	BRUKER APEX-II, φ and ω
$\theta_{\max}$, completeness:	71.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	2587, 1500, 0.025
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1338
$N(\text{param})_{\text{refined}}$:	110
Programs:	Bruker [1], SHELX [2, 3]

Source of material

An aqueous solution (5 mL) of 2'-deoxycytidine-5'-monophosphate (*dCMP*, 30 mg, 0.10 mmol) was added into an aqueous solution (5 mL) of $Co(ClO_4)_2 \cdot 6H_2O$ (18 mg, 0.05 mmol). After stirring for 10 min, 1,2-bis(4-pyridyl)ethane (*bpa*, 9 mg, 0.05 mmol) in distilled water (5 mL) was added to this mixture. Perchloric acid was also dropped in it and the resulting solution (pH = 3) was stirred at room temperature for 30 min. The colorless block crystals of the perchlorate salt of the starting material 1,2-bis(4-pyridyl)ethane were obtained by evaporation at room temperature after two weeks by accident.

Experimental details

The structure was solved by direct methods and refined using the SHELXL programs [2, 3]. The hydrogen atoms were restrained. Their U_{iso} values were set to $1.2U_{\text{eq}}$ of the parent atoms.

Comment

1,2-bis(4-pyridyl)ethane (*bpa*) is a perfect ligand to form supramolecular structures [4–6]. In our previous work [7], we used auxiliary ligands, namely *bpa*, to competitively coordinate a metal ion to a mononucleotide to restrain the nonenzymatic hydrolysis of the phosphate group catalyzed by metal ions, and we got complex $Co\text{-}dCMP\text{-}bpa$

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Abstract

$C_{12}H_{14}N_2 \cdot 2ClO_4$, monoclinic, $P2_1/c$ (no. 14), $a = 5.3170(4)$ Å, $b = 12.8711(8)$ Å, $c = 11.6788(7)$ Å, $\beta = 100.888(2)^\circ$, $V = 784.86(9)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0434$, $wR_{\text{ref}}(F^2) = 0.1211$, $T = 298$ K.

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The asymmetric unit (labeled atoms) of the title crystal 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.

*Corresponding authors: Qi-Ming Qiu and Zhi-Yuan Zheng, School of Science, China University of Geosciences, Beijing 100083, P. R. China, E-mail: qiuqiming890521@163.com (Q.-M. Qiu), zhzyzheng@cugb.edu.cn (Z.-Y. Zheng). <https://orcid.org/0000-0002-1060-8859> (Q.-M. Qiu)

Jian-Biao Song, Beijing Chaoyang Foreign Language School, Beijing 100101, P. R. China

Li Yan, Analytical and Testing Centre, Beijing Institute of Technology, Beijing 100081, P. R. China

Ai-Guo Dong and Chuan-Tao Li, School of Science, China University of Geosciences, Beijing 100083, P. R. China

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

Atom	x	y	z	U _{iso} [*] /U _{eq}
C1	0.3463 (5)	0.9660 (3)	0.8381 (2)	0.0552 (8)
H1A	0.230091	0.985707	0.884468	0.066*
C2	0.3460 (5)	1.0154 (2)	0.7338 (2)	0.0513 (7)
H2	0.229471	1.068425	0.709045	0.062*
C3	0.5219 (5)	0.98538 (19)	0.6653 (2)	0.0408 (6)
C4	0.6890 (5)	0.9061 (2)	0.7074 (2)	0.0441 (6)
H4	0.809190	0.884236	0.664155	0.053*
C5	0.6805 (6)	0.8597 (2)	0.8108 (2)	0.0504 (7)
H5	0.793518	0.806186	0.838106	0.060*
C6	0.5286 (7)	1.0364 (2)	0.5505 (2)	0.0648 (9)
H6A	0.404808	1.092604	0.538650	0.078*
H6B	0.696914	1.066438	0.553110	0.078*
O1	0.4271 (4)	0.70887 (16)	0.57945 (18)	0.0599 (6)
O2	0.0654 (4)	0.60474 (17)	0.5571 (2)	0.0681 (7)
O3	0.1610 (4)	0.71803 (19)	0.71709 (17)	0.0668 (7)
O4	0.0215 (5)	0.78368 (17)	0.5288 (2)	0.0690 (6)
N1	0.5111 (5)	0.89091 (19)	0.87248 (18)	0.0523 (6)
H1	0.508191	0.860886	0.937997	0.063*
Cl1	0.16707 (11)	0.70393 (4)	0.59677 (5)	0.0399 (3)

(dCMP = 2'-deoxycytidine-5'-monophosphate) below pH = 6. Due to the different charged states of dCMP in aqueous solution, it is meaningful to study nucleotide complex in other different pH values. Single crystals of the title compound has been obtained under a more acidic environment (pH = 3).

Polymorphism in crystals is defined as a compound has identical chemical compositions while adopting more than one arrangement [8]. Widely used drugs such as aspirin and acetaminophen are all known to be polymorphic, and the crystal packing of them have a significant impact on their properties [9]. There is a recently reported example of organic polymorphs: 3-ammonio-4-aminobenzoate is found to form two polymorphs [10, 11]. The title compound consists of *bpa* molecules located around a two-fold axes and perchlorate anions in general positions with a ratio of 1:2 (monoclinic space group $P2_1/c$, $Z = 2$). In contrast the reported polymorph (space group $P2_1$, $Z = 4$) [6] consists of two crystallographically independent *bpa* molecules. In the previous polymorph, the distance between two adjacent six membered rings is 4.007(2) and 3.945(3) Å, which shows very weak π - π -stacking interactions [6]. However, in title compound, this value is expanded to 5.613(1) Å, indicating that there is no π - π -stacking interactions in the compound. In addition, neighboring *bpa* molecules are linked by the N1-H1-N2/N3-H3A-N4 to form a one-dimensional chain

expanded along the *b*-axis in the previous polymorph [6], while, the hydrogen bonds in the title structure are weaker.

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