

# Crystal structures of 1,1'-bis(carboxymethyl)-4,4'-bipyridinium derivatives

Hitoshi Kumagai,<sup>a\*</sup> Satoshi Kawata<sup>b</sup> and Nobuhiro Ogihara<sup>a</sup><sup>a</sup>41-1 Yokomichi, Nagakute, Aichi 480-1192, Japan, and <sup>b</sup>Nanakuma Jonan-ku, Fukuoka 814-0180, Japan. \*Correspondence e-mail: e1254@mosk.tytlabs.co.jp

Received 7 May 2024

Accepted 30 May 2024

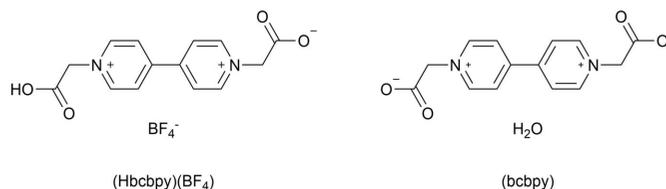
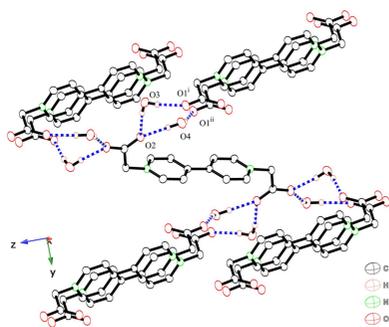
Edited by T. Akitsu, Tokyo University of Science, Japan

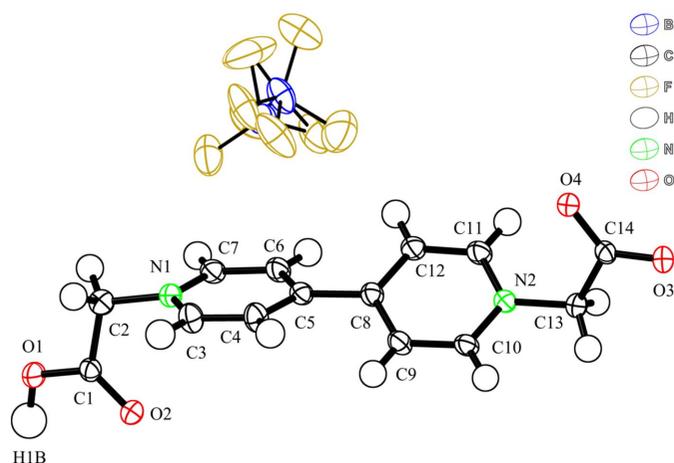
**Keywords:** crystal structure; hydrogen bonding; viologen.**CCDC references:** 2359279; 2359278**Supporting information:** this article has supporting information at journals.iucr.org/e

The crystal structures of 2-[1'-(carboxymethyl)-4,4'-bipyridine-1,1'-dium-1-yl]-acetate tetrafluoroborate,  $C_{14}H_{13}N_2O_4^+ \cdot BF_4^-$  or (Hbcppy)( $BF_4$ ), and neutral 1,1'-bis(carboxylatomethyl)-4,4'-bipyridine-1,1'-dium (bcppy),  $C_{14}H_{20}N_2O_8$ , are reported. The asymmetric unit of the (Hbcppy)( $BF_4$ ) consists of a Hbcppy<sup>+</sup> monocation, a  $BF_4^-$  anion, and one-half of a water molecule. The  $BF_4^-$  anion is disordered. Two pyridinium rings of the Hbcppy<sup>+</sup> monocation are twisted at a torsion angle of 30.3 (2)° with respect to each other. The Hbcppy monocation contains a carboxylic acid group and a deprotonated carboxylate group. Both groups exhibit both a long and a short C—O bond. The cations are linked by intermolecular hydrogen-bonding interactions between the carboxylic acid and the deprotonated carboxylate group to give one-dimensional zigzag chains. The asymmetric unit of the neutral bcppy consists of one-half of the bcppy and two water molecules. In contrast to the Hbcppy<sup>+</sup> monocation, the neutral bcppy molecule contains two pyridinium rings that are coplanar with each other and a carboxylate group with similar C—O bond lengths. The molecules are connected by intermolecular hydrogen-bonding interactions between water molecules and carboxylate groups, forming a three-dimensional hydrogen-bonding network.

## 1. Chemical context

Viologen derivatives (*N,N'*-disubstituted bipyridinium salts) have been widely researched because of their reversible electroactivity, good photochromic properties, and high biochemical activity. Because of these interesting physical and chemical properties, the synthesis of organic polymers or metal–organic frameworks by assembling viologen derivatives using covalent bonds or coordination bonds is attracting attention (Jouhara *et al.*, 2019; Madasamy *et al.*, 2019; Sun & Zhang, 2015). Non-covalent interactions such as hydrogen-bonding and electrostatic interactions have been used to assemble functional molecules in the field of crystal engineering (Desiraju, 2001; Horiuchi *et al.*, 2007; Lehn, 1995). We have been working on hydrogen-bonded assemblies to synthesize functional materials and have previously reported hydrogen-bonded assemblies in which functional molecules such as redox-active ferrocene derivatives or tetrathiafulvalene are used (Kitagawa & Kawata, 2002; Nagayoshi *et al.*, 2003). In the present study, we focus on hydrogen-bonded assemblies of *N,N'*-bis(2-carboxyethyl)-4,4'-bipyridinium derivatives.

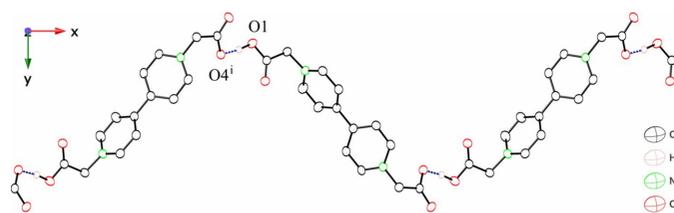




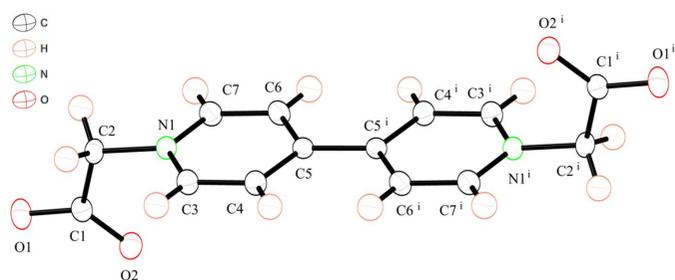
**Figure 1**  
Structure of (Hbcbpy)(BF<sub>4</sub>) with labeling scheme and 50% probability displacement ellipsoids.

## 2. Structural commentary

The asymmetric unit of (Hbcbpy)(BF<sub>4</sub>) consists of a Hbcbpy<sup>+</sup> monocation, a BF<sub>4</sub><sup>−</sup> anion, and one-half of a water molecule (Fig. 1). The BF<sub>4</sub><sup>−</sup> anion is disordered. The key feature of the structure is a hydrogen-bonded one-dimensional chain structure in which the chains are connected by intermolecular  $\text{—COO}^{\cdot\cdot}\cdots\text{HOOC—}$  hydrogen-bonding interactions (Table 1, Fig. 2). Because the water molecules of (Hbcbpy)(BF<sub>4</sub>) are not involved in the hydrogen-bonding interactions, water molecules are easily lost from the crystal to give partial occupancy. Two pyridinium groups of the Hbcbpy<sup>+</sup> monocation are twisted at a C4—C5—C8—C9 torsion angle of 30.3 (2)° [dihedral angle between the rings = 30.18 (8)°] to each other. The carboxymethyl groups bonded to the pyridinium groups exhibit a bent structure and are nearly perpendicular to the pyridinium groups. The Hbcbpy<sup>+</sup> monocation contains a carboxylic acid group,  $\text{—COOH}$ , and a deprotonated negatively charged carboxylate group,  $\text{—COO}^{\cdot\cdot}$ , at each end of the monocation. The charge is compensated by a BF<sub>4</sub><sup>−</sup> anion. The C—O and C=O bond lengths in the carboxylic acid group, C1—O1 and C1—O2, are 1.294 (2) and 1.223 (2) Å, respectively, with a difference of 0.071 (2) Å. Although the carboxylate group is deprotonated, C14—O3 and C14—O4 also show two different bond lengths of 1.235 (2) and 1.287 (2) Å, respectively, where the difference is 0.052 (2) Å.



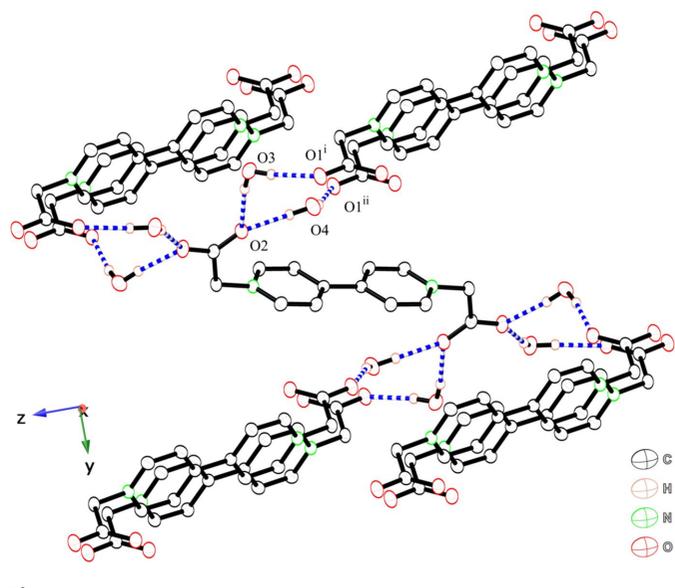
**Figure 2**  
View of the hydrogen-bonded zigzag chain structure of Hbcbpy<sup>+</sup> monocations. Dashed lines represent hydrogen bonds between oxygen atoms of Hbcbpy<sup>+</sup> monocations. Only the carboxylic hydrogen atoms are shown for clarity. [Symmetry code: (i)  $x - \frac{9}{2}, -y - \frac{7}{2}, z - \frac{7}{2}$ ]



**Figure 3**  
Structure of bcbpy with labeling scheme and 50% probability displacement ellipsoids. [Symmetry code: (i)  $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ ]

The carboxylic acid group acts as a hydrogen-bond donor, and O4 of the deprotonated carboxylate groups acts as a hydrogen-bond acceptor; the C14—O4 bond is longer than the C14—O3 bond. No hydrogen-bonding interactions are found for O3. The corresponding ClO<sub>4</sub><sup>−</sup> salt also exhibits two different C—O bond lengths in the deprotonated carboxylate group and similar hydrogen-bonding interactions to give a zigzag chain structure (Gutov *et al.*, 2008). While the measurements of the (Hbcbpy)(BF<sub>4</sub>) were conducted at 100 K, the hydrogen-bonding distances of O(carboxylic acid)⋯O(carboxylate) is very similar to that of the ClO<sub>4</sub> salt measured at room temperature, indicative of a small influence of thermal libration (Gutov *et al.*, 2008). We assume that the different C—O bond lengths in the carboxylate group arise from intermolecular hydrogen-bonding interactions.

The asymmetric unit of bcbpy consists of one-half of the neutral bcbpy molecule and two solvent water molecules (Fig. 3). The key feature of the structure is a hydrogen-bonded three-dimensional network in which the molecules are connected by intermolecular hydrogen bonding interactions



**Figure 4**  
View of hydrogen-bonded network of bcbpy molecules and water molecules. Dashed lines represent hydrogen bonds between oxygen atoms. Hydrogen atoms of bcbpy are omitted for clarity. Only the hydrogen atoms of the water molecules are shown for clarity. [Symmetry codes: (i)  $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (ii)  $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ ]

**Table 1**Hydrogen-bond geometry (Å, °) for (Hbcbpy)(BF<sub>4</sub>).

| <i>D</i> —H··· <i>A</i>  | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|--------------------------|-------------|---------------|-----------------------|-------------------------|
| O1—H1B···O4 <sup>i</sup> | 1.05        | 1.42          | 2.4694 (18)           | 172.0                   |

Symmetry code: (i)  $x - \frac{9}{2}, -y - \frac{7}{2}, z - \frac{7}{2}$ .

between bcbpy and water molecules (Table 2, Fig. 4). In the bcbpy molecule, two negatively charged deprotonated carboxylate groups are attached to the pyridinium groups to give a neutral molecule. The carboxymethyl group bonded to the pyridinium group exhibits a structure similar to that of a Hbcbpy<sup>+</sup> monocation. Two C—O bonds in the carboxylate group form similar hydrogen-bonding interactions between water molecules. Two differences are observed between the structure of the bcbpy molecule and that of the Hbcbpy<sup>+</sup> monocation. The first difference is the arrangement of the two pyridinium groups. Although the two pyridinium groups are twisted toward each other in the Hbcbpy<sup>+</sup> monocation, they are coplanar with each other in the neutral bcbpy molecule, with a C6—C5—C5<sup>i</sup>—C4<sup>i</sup> torsion angle of 0.31 (14)°. The other difference is the C—O bond lengths in the deprotonated carboxylate group. In the neutral bcbpy molecule, the two C—O bond lengths are similar [1.248 (1) and 1.255 (1) Å, and the difference [0.007 (1) Å] is smaller than that between the C—O bond lengths in the deprotonated carboxylate group in the Hbcbpy<sup>+</sup> monocation. Both C—O bonds in the carboxylate group undergo similar hydrogen-bonding interactions between water molecules (Fig. 4). A neutral bcbpy molecule without coordination bonds has been reported in [Zn(H<sub>2</sub>O)<sub>6</sub>](bcbpy)·(1,4-benzenedicarboxylate)·3H<sub>2</sub>O (Zhao & Liu, 2021). The bcbpy molecule in this Zn compound contains two types of carboxylate groups. One carboxylate group shows hydrogen-bonding interactions similar to those observed in our structure; the two C—O bond lengths in the carboxylate group are 1.236 (3) and 1.249 (3) Å, differing by 0.013 (3) Å. The other carboxylate group in the Zn compound exhibits two types of hydrogen-bonding interactions: interactions with three water molecules, and an interaction with one water molecule. The two C—O bond lengths in the carboxylate group are 1.235 (3) and 1.259 (3) Å; thus, the difference between the C—O bond lengths [0.024 (3) Å] is slightly larger than the corresponding difference for the first carboxylate group. These results indicate that the difference between the two C—O bond lengths in the carboxylate group is influenced by the type of hydrogen-bonding interactions in the bcbpy system.

### 3. Supramolecular features

The Hbcbpy<sup>+</sup> monocation contains a carboxylic acid and a deprotonated carboxylate group at each end of the monocation. Intermolecular hydrogen-bonding interactions occur between the carboxylic acid of one cation and the negatively charged carboxylate groups of another monocation to give one-dimensional chains (Table 1, Fig. 2). The chains zigzag because of the bent structure of the carboxymethyl groups

**Table 2**

Hydrogen-bond geometry (Å, °) for bcbpy.

| <i>D</i> —H··· <i>A</i>   | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| O3—H9···O2                | 0.859 (19)  | 1.96 (2)      | 2.8135 (12)           | 172.1 (19)              |
| O3—H8···O1 <sup>i</sup>   | 0.85 (2)    | 1.95 (2)      | 2.7888 (11)           | 171 (2)                 |
| O4—H10···O2               | 0.89 (2)    | 1.97 (2)      | 2.8233 (12)           | 158.9 (18)              |
| O4—H11···O1 <sup>ii</sup> | 0.85 (2)    | 1.97 (2)      | 2.8007 (13)           | 164.1 (17)              |

Symmetry codes: (i)  $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (ii)  $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ .

attached to the pyridinium groups. Within the chains, the pyridinium rings are not coplanar, exhibiting no  $\pi$ – $\pi$  stacking interactions.

The bcbpy molecule contains two deprotonated carboxylate groups at its ends. The negatively charged carboxylate groups undergo intermolecular hydrogen-bonding interactions between water molecules (Table 2). The negatively charged carboxylate groups act as hydrogen-bond acceptors, and water molecules act as hydrogen-bond donors. The water molecule bridges two bcbpy molecules by hydrogen-bonding interactions, forming a three-dimensional hydrogen bonding network. Although the two pyridinium groups are coplanar, no  $\pi$ – $\pi$  stacking interactions are observed.

Both compounds lack  $\pi$ – $\pi$  stacking interactions. A possible explanation for this is that the carboxymethyl groups bonded to the pyridinium groups, which are bent and nearly perpendicular to the pyridinium groups, prevent stacking interactions. Thus, the supramolecular structures of the Hbcbpy<sup>+</sup> monocation and bcbpy molecule are primarily stabilized by the hydrogen-bonding interactions between negatively charged carboxylate groups and carboxylic acids or water molecules.

### 4. Database survey

A survey of the Cambridge Structural Database (CSD, v5.44, April 2023; Groom *et al.*, 2016) for structures with a bcbpy moiety resulted in nine matches. Of these, (Hbcbpy)(ClO<sub>4</sub>) (ODOQUV; Zhao & Liu, 2021) and (Zn(H<sub>2</sub>O)<sub>6</sub>)(bcbpy)(1,4-benzenedicarboxylate) (AXEJJEV; Gutov *et al.*, 2008) are related to the present work. Other compounds exhibit metal coordination and contain co-bridging ligands such as tricarboxylate or hexacyano metallate ions to compensate charges (Li *et al.*, 2020; Liu *et al.*, 2020; Ma *et al.*, 2009, 2011). The crystal structures of similar viologens in which carboxyethyl groups are attached to nitrogen atoms have been reported, *viz.* 3-[1'-(2-carboxyethyl)-4,4'-bipyridinium-1-yl]propanoate perchlorate (ODOQOP; Gutov *et al.*, 2008) and *catena*-[tris[1,1'-bis(2-carboxyethyl)-4,4'-bipyridinium]hexakis( $\mu$ -bromo)tribromotrilead(II) dihydrate] (FEBLOQ; Sun *et al.*, 2017). ODOQOP is a monocation similar to ODOQUV. FEBLOQ is a dication in which [Pb<sub>3</sub>Br<sub>9</sub>]<sub>n</sub><sup>3n-</sup> chains act as counter-ions in the crystal. (4-[2-[1-(Carboxymethyl)pyridin-1-ium-4-yl]ethenyl]pyridin-1-ium-1-yl)acetate tetrafluoroborate (MUPBUX), (4-[2-[1-(carboxymethyl)pyridin-1-ium-4-yl]ethenyl]pyridin-1-ium-1-yl)acetate perchlorate (MUPCAE), and tris(aqua)-[1-(carboxymethyl)-4-(2-[1-[(carboxy)methyl]pyridin-1-ium-4-yl]ethenyl)pyridin-1-iumato]lithium iodide

dihydrate (MUPCEI) are ethylenic derivatives in which two pyridinium groups are linked by an ethylene group (Jouhara *et al.*, 2019). MUPBUX and MUPCAE are monocations similar to the Hbcbpy<sup>+</sup> monocation.

### 5. Synthesis and crystallization

The dibromo salt H<sub>2</sub>bcbpy(Br)<sub>2</sub> was synthesized using a modified version of a reported procedure (Fajardo & Lewis, 1997). The route is presented in the supporting information (scheme S1). (Hbcbpy)(BF<sub>4</sub>) and bcbpy were obtained as follows. An aqueous solution (50 mL) of Li(BF<sub>4</sub>) (38.6 g, 320 mmol) was added to an aqueous solution (50 mL) of H<sub>2</sub>bcbpy(Br)<sub>2</sub> (20.0 g, 40 mmol). The mixture was stirred, the resultant white precipitate was collected by filtration, and the obtained solution was slowly evaporated to yield colorless crystals of (Hbcbpy)(BF<sub>4</sub>). The crystals (4.9 g, 11 mmol) were dissolved in 30 mL of distilled water, and an aqueous solution (20 mL) of LiOH (0.42 g, 18 mmol) was added. The resultant solution was evaporated, and the obtained white precipitate was filtered. Colorless crystals began to form from the obtained solution at ambient temperature. One of these crystals was used for X-ray crystallographic analysis.

### 6. Refinement

The crystal data, data collection, and structure refinement details are summarized in Table 3. The hydrogen atoms of the carboxylic acid and water molecules, which are involved in hydrogen-bonding interactions were located in difference-Fourier maps and refined isotropically. Other hydrogen atoms were placed in idealized positions and refined using a riding model. The occupancy of the water molecule in (Hbcbpy)(BF<sub>4</sub>) was refined.

### Acknowledgements

We would like to thank Dr Mitsutaro Umehara for help with the database survey.

### References

- Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G., Siliqi, D. & Spagna, R. (2007). *J. Appl. Cryst.* **40**, 609–613.
- Desiraju, G. R. (2001). *Nature*, **412**, 397–400.
- Fajardo, A. M. & Lewis, N. S. (1997). *J. Phys. Chem. B*, **101**, 11136–11151.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Gutov, A. V., Rusanov, E. B., Yegorov, O. A. & Gernega, A. N. (2008). *Zh. Org. Farm. Khim.* **6**, 46–48.
- Horiuchi, S., Kumai, R. & Tokura, Y. (2007). *Chem. Commun.* pp. 2321–2329.
- Jouhara, A., Quarez, E., Dolhem, F., Armand, M., Dupré, N. & Poizot, P. (2019). *Angew. Chem. Int. Ed.* **58**, 15680–15684.
- Kabuto, C., Akine, S., Nemoto, T. & Kwon, E. (2009). *J. Crystallogr. Soc. Jpn.* **51**, 218–224.
- Kitagawa, S. & Kawata, S. (2002). *Coord. Chem. Rev.* **224**, 11–34.
- Lehn, J.-M. (1995). *Supramolecular Chemistry, Concepts and Perspectives*. Weinheim, Germany: VCH.
- Li, M. H., Lv, S. L., You, M. H. & Lin, M. J. (2020). *Dalton Trans.* **49**, 13083–13089.
- Liu, J. J., Lu, Y. W. & Lu, W. B. (2020). *Dyes and Pigments*, **180**, 108498.
- Ma, Y., Bandeira, N. A. G., Robert, V. & Gao, E. Q. (2011). *Chem. Eur. J.* **17**, 1988–1998.
- Ma, Y., Zhang, J. Y., Cheng, A. L., Sun, Q., Gao, E. Q. & Liu, C. M. (2009). *Inorg. Chem.* **48**, 6142–6151.
- Madasamy, K., Velayutham, D., Suryanarayanan, V., Kathiresan, M. & Ho, K. C. (2019). *J. Mater. Chem. C*, **7**, 4622–4637.
- Nagayoshi, K., Kabir, M. K., Tobita, H., Honda, K., Kawahara, M., Katada, M., Adachi, K., Nishikawa, H., Ikemoto, I., Kumagai, H., Hosokoshi, Y., Inoue, K., Kitagawa, S. & Kawata, S. (2003). *J. Am. Chem. Soc.* **125**, 221–232.
- Palatinus, L. & Chapuis, G. (2007). *J. Appl. Cryst.* **40**, 786–790.
- Rigaku (1995). *ABSCOR and RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku (2019). *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Sun, C., Wang, M. S., Zhang, X., Zhang, N. N., Cai, L. R. & Guo, G. C. (2017). *CrystEngComm*, **19**, 4476–4479.
- Sun, J. K. & Zhang, J. (2015). *Dalton Trans.* **44**, 19041–19055.
- Zhao, G. Z. & Liu, J. J. (2021). *RSC Adv.* **11**, 24500–24507.

## supporting information

*Acta Cryst.* (2024). E80, 695-698 [https://doi.org/10.1107/S2056989024005127]

## Crystal structures of 1,1'-bis(carboxymethyl)-4,4'-bipyridinium derivatives

Hitoshi Kumagai, Satoshi Kawata and Nobuhiro Ogihara

## Computing details

## 1,1'-Bis(carboxylatomethyl)-4,4'-bipyridine-1,1'-dium (bcbpy)

*Crystal data*

$C_{14}H_{20}N_2O_8$

$M_r = 344.32$

Monoclinic,  $P2_1/n$

$a = 6.2521$  (2) Å

$b = 11.4122$  (4) Å

$c = 11.1413$  (4) Å

$\beta = 99.4832$  (14)°

$V = 784.07$  (5) Å<sup>3</sup>

$Z = 2$

$F(000) = 364.00$

$D_x = 1.458$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71075$  Å

Cell parameters from 7055 reflections

$\theta = 3.3$ – $27.5$ °

$\mu = 0.12$  mm<sup>-1</sup>

$T = 296$  K

Block, yellow

$0.48 \times 0.46 \times 0.42$  mm

*Data collection*

Rigaku R-AXIS RAPID

diffractometer

Detector resolution: 10.000 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan

(ABSCOR; Rigaku, 1995)

$T_{\min} = 0.788$ ,  $T_{\max} = 0.951$

7476 measured reflections

1793 independent reflections

1678 reflections with  $F^2 > 2.0\sigma(F^2)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 27.5$ °,  $\theta_{\min} = 3.5$ °

$h = -8 \rightarrow 7$

$k = -14 \rightarrow 14$

$l = -14 \rightarrow 14$

*Refinement*

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.123$

$S = 1.11$

1793 reflections

125 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0813P)^2 + 0.1761P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.40$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.28$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on  $F^2$ . R-factor (gt) are based on F. The threshold expression of  $F^2 > 2.0 \sigma(F^2)$  is used only for calculating R-factor (gt).

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

|     | <i>x</i>      | <i>y</i>     | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|--------------|--------------|----------------------------------|
| O1  | 0.51613 (14)  | 0.68508 (8)  | 0.03041 (7)  | 0.0252 (2)                       |
| O2  | 0.48570 (13)  | 0.70887 (7)  | 0.22699 (7)  | 0.0228 (2)                       |
| O3  | 0.80684 (15)  | 0.87902 (8)  | 0.29910 (8)  | 0.0270 (2)                       |
| O4  | 0.41417 (14)  | 0.74797 (8)  | 0.46745 (8)  | 0.0277 (2)                       |
| N1  | 0.17838 (14)  | 0.54278 (8)  | 0.22070 (8)  | 0.0176 (2)                       |
| C7  | 0.28870 (17)  | 0.46929 (10) | 0.30354 (10) | 0.0207 (3)                       |
| H7  | 0.411238      | 0.430906     | 0.286205     | 0.025*                           |
| C6  | 0.22108 (18)  | 0.45072 (9)  | 0.41363 (10) | 0.0204 (3)                       |
| H6  | 0.297168      | 0.399296     | 0.469856     | 0.025*                           |
| C5  | 0.03839 (16)  | 0.50899 (9)  | 0.44103 (9)  | 0.0165 (3)                       |
| C4  | -0.07103 (17) | 0.58473 (10) | 0.35318 (9)  | 0.0194 (3)                       |
| H4  | -0.193261     | 0.624817     | 0.368421     | 0.023*                           |
| C3  | 0.00173 (17)  | 0.60021 (10) | 0.24390 (10) | 0.0199 (3)                       |
| H3  | -0.071887     | 0.650736     | 0.185822     | 0.024*                           |
| C2  | 0.26195 (17)  | 0.56648 (10) | 0.10675 (9)  | 0.0195 (3)                       |
| H2A | 0.143316      | 0.591106     | 0.044479     | 0.023*                           |
| H2B | 0.322475      | 0.495057     | 0.079110     | 0.023*                           |
| C1  | 0.43789 (17)  | 0.66260 (9)  | 0.12460 (9)  | 0.0183 (2)                       |
| H9  | 0.709 (3)     | 0.8291 (18)  | 0.2700 (17)  | 0.041 (5)*                       |
| H8  | 0.860 (3)     | 0.8538 (18)  | 0.369 (2)    | 0.049 (5)*                       |
| H10 | 0.400 (3)     | 0.7365 (16)  | 0.387 (2)    | 0.041 (5)*                       |
| H11 | 0.285 (3)     | 0.7551 (15)  | 0.4820 (18)  | 0.043 (5)*                       |

*Atomic displacement parameters ( $\text{\AA}^2$ )*

|    | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$    | $U^{13}$   | $U^{23}$    |
|----|------------|------------|------------|-------------|------------|-------------|
| O1 | 0.0241 (4) | 0.0337 (5) | 0.0190 (4) | -0.0043 (3) | 0.0071 (3) | 0.0034 (3)  |
| O2 | 0.0228 (4) | 0.0264 (4) | 0.0193 (4) | -0.0036 (3) | 0.0037 (3) | -0.0010 (3) |
| O3 | 0.0265 (5) | 0.0282 (5) | 0.0259 (5) | -0.0060 (3) | 0.0033 (3) | 0.0055 (3)  |
| O4 | 0.0210 (5) | 0.0380 (5) | 0.0241 (5) | 0.0000 (3)  | 0.0041 (3) | -0.0065 (4) |
| N1 | 0.0185 (5) | 0.0185 (4) | 0.0162 (4) | -0.0025 (3) | 0.0045 (3) | 0.0000 (3)  |
| C7 | 0.0206 (5) | 0.0204 (5) | 0.0221 (5) | 0.0028 (4)  | 0.0067 (4) | 0.0023 (4)  |
| C6 | 0.0215 (5) | 0.0198 (5) | 0.0209 (5) | 0.0032 (4)  | 0.0059 (4) | 0.0039 (4)  |
| C5 | 0.0173 (5) | 0.0155 (5) | 0.0171 (5) | -0.0023 (4) | 0.0037 (4) | -0.0004 (4) |
| C4 | 0.0180 (5) | 0.0212 (5) | 0.0193 (5) | 0.0016 (4)  | 0.0045 (4) | 0.0013 (4)  |
| C3 | 0.0191 (5) | 0.0219 (5) | 0.0186 (5) | 0.0016 (4)  | 0.0029 (4) | 0.0025 (4)  |
| C2 | 0.0214 (5) | 0.0230 (5) | 0.0151 (5) | -0.0017 (4) | 0.0058 (4) | -0.0003 (4) |
| C1 | 0.0162 (5) | 0.0209 (5) | 0.0182 (5) | 0.0013 (4)  | 0.0035 (4) | 0.0026 (4)  |

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

|                           |              |                    |              |
|---------------------------|--------------|--------------------|--------------|
| O1—C1                     | 1.2553 (13)  | C6—C5              | 1.3982 (14)  |
| O2—C1                     | 1.2479 (14)  | C6—H6              | 0.9300       |
| O3—H9                     | 0.86 (2)     | C5—C4              | 1.3973 (15)  |
| O3—H8                     | 0.85 (2)     | C5—C5 <sup>i</sup> | 1.4856 (19)  |
| O4—H10                    | 0.89 (2)     | C4—C3              | 1.3794 (14)  |
| O4—H11                    | 0.85 (2)     | C4—H4              | 0.9300       |
| N1—C3                     | 1.3454 (14)  | C3—H3              | 0.9300       |
| N1—C7                     | 1.3495 (15)  | C2—C1              | 1.5429 (15)  |
| N1—C2                     | 1.4753 (13)  | C2—H2A             | 0.9700       |
| C7—C6                     | 1.3780 (14)  | C2—H2B             | 0.9700       |
| C7—H7                     | 0.9300       |                    |              |
| H9—O3—H8                  | 105.7 (19)   | C3—C4—H4           | 119.9        |
| H10—O4—H11                | 105.3 (18)   | C5—C4—H4           | 119.9        |
| C3—N1—C7                  | 120.97 (9)   | N1—C3—C4           | 120.51 (10)  |
| C3—N1—C2                  | 119.62 (9)   | N1—C3—H3           | 119.7        |
| C7—N1—C2                  | 119.27 (9)   | C4—C3—H3           | 119.7        |
| N1—C7—C6                  | 120.47 (10)  | N1—C2—C1           | 111.44 (8)   |
| N1—C7—H7                  | 119.8        | N1—C2—H2A          | 109.3        |
| C6—C7—H7                  | 119.8        | C1—C2—H2A          | 109.3        |
| C7—C6—C5                  | 120.17 (10)  | N1—C2—H2B          | 109.3        |
| C7—C6—H6                  | 119.9        | C1—C2—H2B          | 109.3        |
| C5—C6—H6                  | 119.9        | H2A—C2—H2B         | 108.0        |
| C4—C5—C6                  | 117.68 (9)   | O2—C1—O1           | 127.60 (10)  |
| C4—C5—C5 <sup>i</sup>     | 120.85 (11)  | O2—C1—C2           | 118.49 (9)   |
| C6—C5—C5 <sup>i</sup>     | 121.47 (12)  | O1—C1—C2           | 113.91 (9)   |
| C3—C4—C5                  | 120.19 (10)  |                    |              |
| C3—N1—C7—C6               | 0.60 (17)    | C7—N1—C3—C4        | -0.25 (16)   |
| C2—N1—C7—C6               | 176.33 (10)  | C2—N1—C3—C4        | -175.96 (10) |
| N1—C7—C6—C5               | -0.68 (17)   | C5—C4—C3—N1        | -0.02 (17)   |
| C7—C6—C5—C4               | 0.41 (16)    | C3—N1—C2—C1        | 92.74 (11)   |
| C7—C6—C5—C5 <sup>i</sup>  | -179.89 (11) | C7—N1—C2—C1        | -83.05 (12)  |
| C6—C5—C4—C3               | -0.07 (16)   | N1—C2—C1—O2        | -1.12 (14)   |
| C5 <sup>i</sup> —C5—C4—C3 | -179.76 (11) | N1—C2—C1—O1        | 179.23 (9)   |

Symmetry code: (i)  $-x, -y+1, -z+1$ .Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

| $D-H\cdots A$                     | $D-H$      | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|------------|-------------|-------------|---------------|
| O3—H9 $\cdots$ O2                 | 0.859 (19) | 1.96 (2)    | 2.8135 (12) | 172.1 (19)    |
| O3—H8 $\cdots$ O1 <sup>ii</sup>   | 0.85 (2)   | 1.95 (2)    | 2.7888 (11) | 171 (2)       |
| O4—H10 $\cdots$ O2                | 0.89 (2)   | 1.97 (2)    | 2.8233 (12) | 158.9 (18)    |
| O4—H11 $\cdots$ O1 <sup>iii</sup> | 0.85 (2)   | 1.97 (2)    | 2.8007 (13) | 164.1 (17)    |

Symmetry codes: (ii)  $x+1/2, -y+3/2, z+1/2$ ; (iii)  $x-1/2, -y+3/2, z+1/2$ .

2-[1'-(Carboxymethyl)-4,4'-bipyridine-1,1'-diium-1-yl]acetate tetrafluoroborate (Hbc bpyBF<sub>4</sub>)*Crystal data*C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>O<sub>4.5</sub><sup>+</sup>·BF<sub>4</sub><sup>-</sup> $M_r = 368.08$ Monoclinic,  $P2_1/n$  $a = 7.6794$  (16) Å $b = 20.987$  (4) Å $c = 10.0514$  (19) Å $\beta = 95.123$  (3)° $V = 1613.5$  (5) Å<sup>3</sup> $Z = 4$  $F(000) = 756$  $D_x = 1.519$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71075$  Å

Cell parameters from 2543 reflections

 $\theta = 5.6$ – $27.4$ ° $\mu = 0.14$  mm<sup>-1</sup> $T = 100$  K

Platelet, colorless

 $0.60 \times 0.40 \times 0.40$  mm*Data collection*

Rigaku R-AXIS RAPID

diffractometer

Detector resolution: 10.000 pixels mm<sup>-1</sup> $\omega$  scans

Absorption correction: multi-scan

(ABSCOR; Rigaku, 1995)

 $T_{\min} = 0.656$ ,  $T_{\max} = 0.987$ 

15631 measured reflections

3652 independent reflections

3119 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.032$  $\theta_{\max} = 27.4$ °,  $\theta_{\min} = 3.2$ ° $h = -9 \rightarrow 9$  $k = -27 \rightarrow 27$  $l = -13 \rightarrow 13$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.051$  $wR(F^2) = 0.132$  $S = 1.05$ 

3652 reflections

292 parameters

1 restraint

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.0594P)^2 + 1.2013P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} < 0.001$  $\Delta\rho_{\max} = 0.72$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.56$  e Å<sup>-3</sup>*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)*

|      | <i>x</i>      | <i>y</i>    | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|---------------|-------------|--------------|----------------------------------|-----------|
| O4   | -0.12434 (15) | 0.59508 (5) | 0.51560 (12) | 0.0246 (3)                       |           |
| O3   | -0.18392 (15) | 0.49606 (6) | 0.58466 (13) | 0.0278 (3)                       |           |
| C14  | -0.0977 (2)   | 0.54581 (7) | 0.59083 (16) | 0.0212 (3)                       |           |
| C13  | 0.0546 (2)    | 0.54866 (8) | 0.69960 (17) | 0.0232 (3)                       |           |
| H13  | 0.006964      | 0.550938    | 0.787824     | 0.028*                           |           |
| H13A | 0.123093      | 0.508798    | 0.697034     | 0.028*                           |           |
| N2   | 0.17293 (17)  | 0.60349 (6) | 0.68628 (13) | 0.0206 (3)                       |           |
| C10  | 0.3334 (2)    | 0.59435 (8) | 0.64492 (17) | 0.0224 (3)                       |           |
| H10  | 0.368960      | 0.552814    | 0.621280     | 0.027*                           |           |

|     |              |              |              |             |           |
|-----|--------------|--------------|--------------|-------------|-----------|
| C9  | 0.4466 (2)   | 0.64527 (8)  | 0.63679 (17) | 0.0233 (3)  |           |
| H9  | 0.559646     | 0.638678     | 0.607859     | 0.028*      |           |
| C8  | 0.3941 (2)   | 0.70639 (8)  | 0.67125 (16) | 0.0211 (3)  |           |
| C5  | 0.5167 (2)   | 0.76126 (8)  | 0.67427 (16) | 0.0221 (3)  |           |
| N1  | 0.75008 (18) | 0.86160 (6)  | 0.68917 (14) | 0.0227 (3)  |           |
| C12 | 0.2245 (2)   | 0.71446 (8)  | 0.70921 (17) | 0.0249 (4)  |           |
| H12 | 0.183872     | 0.755753     | 0.729713     | 0.030*      |           |
| C7  | 0.6207 (2)   | 0.86054 (8)  | 0.77144 (18) | 0.0252 (3)  |           |
| H7  | 0.611023     | 0.894042     | 0.833916     | 0.030*      |           |
| C1  | 1.0355 (2)   | 0.88901 (7)  | 0.80414 (16) | 0.0208 (3)  |           |
| O1  | 1.14297 (16) | 0.93451 (6)  | 0.84102 (13) | 0.0305 (3)  |           |
| O2  | 1.04698 (15) | 0.83348 (5)  | 0.84064 (12) | 0.0240 (3)  |           |
| C11 | 0.1169 (2)   | 0.66241 (8)  | 0.71677 (17) | 0.0246 (3)  |           |
| H11 | 0.002372     | 0.667885     | 0.743615     | 0.029*      |           |
| C6  | 0.5025 (2)   | 0.81110 (8)  | 0.76520 (17) | 0.0250 (3)  |           |
| H6  | 0.410968     | 0.810802     | 0.822826     | 0.030*      |           |
| C2  | 0.8844 (2)   | 0.91214 (8)  | 0.70692 (18) | 0.0246 (3)  |           |
| H2  | 0.832748     | 0.951166     | 0.742328     | 0.029*      |           |
| H2A | 0.927993     | 0.922573     | 0.619744     | 0.029*      |           |
| F1A | 0.2612 (3)   | 0.83677 (18) | 0.3422 (3)   | 0.0623 (9)  | 0.662 (3) |
| C4  | 0.6512 (2)   | 0.76409 (8)  | 0.58975 (17) | 0.0272 (4)  |           |
| H4  | 0.663465     | 0.731336     | 0.526009     | 0.033*      |           |
| F2A | 0.1745 (3)   | 0.84329 (14) | 0.5476 (2)   | 0.0524 (7)  | 0.662 (3) |
| C3  | 0.7663 (2)   | 0.81476 (9)  | 0.59933 (18) | 0.0283 (4)  |           |
| H3  | 0.858056     | 0.816631     | 0.541966     | 0.034*      |           |
| B1A | 0.2445 (7)   | 0.8769 (2)   | 0.4484 (4)   | 0.0336 (9)  | 0.662 (3) |
| F3A | 0.4096 (3)   | 0.89999 (11) | 0.4970 (2)   | 0.0540 (7)  | 0.662 (3) |
| F4A | 0.1333 (5)   | 0.92664 (13) | 0.4093 (3)   | 0.0938 (13) | 0.662 (3) |
| B1B | 0.1633 (13)  | 0.8772 (5)   | 0.4399 (9)   | 0.037 (2)   | 0.338 (3) |
| H1B | -0.259900    | 0.581900     | 0.413100     | 0.050*      |           |
| F1B | 0.2530 (6)   | 0.9024 (3)   | 0.5528 (4)   | 0.0615 (15) | 0.338 (3) |
| F2B | 0.2596 (6)   | 0.8794 (4)   | 0.3323 (4)   | 0.0537 (15) | 0.338 (3) |
| F3B | 0.1320 (8)   | 0.8129 (3)   | 0.4697 (7)   | 0.0718 (17) | 0.338 (3) |
| F4B | 0.0007 (6)   | 0.9038 (2)   | 0.4137 (3)   | 0.0508 (13) | 0.338 (3) |
| O5B | 0.5838 (6)   | 0.9583 (2)   | 0.5161 (4)   | 0.0446 (11) | 0.352 (2) |
| O5A | -0.1551 (12) | 0.9609 (5)   | 0.4223 (9)   | 0.036 (2)   | 0.148 (2) |

Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$    | $U^{13}$    | $U^{23}$    |
|-----|------------|------------|------------|-------------|-------------|-------------|
| O4  | 0.0198 (6) | 0.0195 (6) | 0.0340 (6) | -0.0016 (4) | -0.0005 (5) | 0.0036 (5)  |
| O3  | 0.0219 (6) | 0.0218 (6) | 0.0396 (7) | -0.0056 (5) | 0.0020 (5)  | 0.0037 (5)  |
| C14 | 0.0158 (7) | 0.0200 (7) | 0.0285 (8) | -0.0005 (6) | 0.0057 (6)  | -0.0001 (6) |
| C13 | 0.0203 (8) | 0.0192 (7) | 0.0303 (8) | -0.0010 (6) | 0.0034 (6)  | 0.0037 (6)  |
| N2  | 0.0172 (6) | 0.0193 (6) | 0.0251 (7) | -0.0003 (5) | 0.0008 (5)  | -0.0002 (5) |
| C10 | 0.0166 (7) | 0.0206 (7) | 0.0297 (8) | 0.0028 (6)  | 0.0005 (6)  | -0.0042 (6) |
| C9  | 0.0168 (7) | 0.0238 (8) | 0.0294 (8) | 0.0001 (6)  | 0.0024 (6)  | -0.0057 (6) |
| C8  | 0.0192 (7) | 0.0204 (8) | 0.0236 (7) | -0.0014 (6) | 0.0002 (6)  | -0.0026 (6) |

|     |             |             |             |              |              |              |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C5  | 0.0183 (7)  | 0.0201 (7)  | 0.0273 (8)  | -0.0001 (6)  | -0.0016 (6)  | -0.0016 (6)  |
| N1  | 0.0200 (7)  | 0.0181 (6)  | 0.0294 (7)  | -0.0015 (5)  | -0.0019 (5)  | -0.0004 (5)  |
| C12 | 0.0213 (8)  | 0.0194 (8)  | 0.0339 (9)  | 0.0018 (6)   | 0.0022 (6)   | -0.0047 (7)  |
| C7  | 0.0216 (8)  | 0.0204 (8)  | 0.0330 (9)  | 0.0016 (6)   | 0.0005 (6)   | -0.0059 (7)  |
| C1  | 0.0185 (7)  | 0.0186 (7)  | 0.0260 (8)  | -0.0003 (6)  | 0.0053 (6)   | -0.0016 (6)  |
| O1  | 0.0262 (6)  | 0.0195 (6)  | 0.0438 (7)  | -0.0050 (5)  | -0.0087 (5)  | 0.0016 (5)   |
| O2  | 0.0231 (6)  | 0.0179 (6)  | 0.0311 (6)  | -0.0008 (4)  | 0.0021 (5)   | 0.0012 (5)   |
| C11 | 0.0190 (8)  | 0.0229 (8)  | 0.0322 (8)  | 0.0025 (6)   | 0.0046 (6)   | -0.0045 (7)  |
| C6  | 0.0198 (8)  | 0.0229 (8)  | 0.0325 (9)  | 0.0007 (6)   | 0.0041 (6)   | -0.0048 (7)  |
| C2  | 0.0216 (8)  | 0.0176 (7)  | 0.0338 (9)  | -0.0031 (6)  | -0.0011 (6)  | 0.0010 (6)   |
| F1A | 0.0304 (11) | 0.099 (2)   | 0.0589 (15) | -0.0085 (14) | 0.0125 (10)  | -0.0396 (17) |
| C4  | 0.0267 (9)  | 0.0260 (8)  | 0.0291 (8)  | -0.0052 (7)  | 0.0044 (7)   | -0.0081 (7)  |
| F2A | 0.0353 (11) | 0.0829 (18) | 0.0405 (11) | -0.0104 (11) | 0.0127 (9)   | 0.0096 (12)  |
| C3  | 0.0265 (9)  | 0.0294 (9)  | 0.0294 (9)  | -0.0051 (7)  | 0.0054 (7)   | -0.0055 (7)  |
| B1A | 0.034 (2)   | 0.0352 (19) | 0.032 (2)   | 0.000 (2)    | 0.007 (2)    | 0.0040 (14)  |
| F3A | 0.0532 (13) | 0.0619 (14) | 0.0449 (11) | -0.0261 (10) | -0.0073 (9)  | 0.0120 (10)  |
| F4A | 0.122 (3)   | 0.0458 (15) | 0.103 (2)   | 0.0258 (17)  | -0.054 (2)   | 0.0037 (14)  |
| B1B | 0.028 (4)   | 0.058 (5)   | 0.026 (4)   | -0.009 (5)   | 0.011 (4)    | -0.004 (3)   |
| F1B | 0.049 (3)   | 0.100 (4)   | 0.034 (2)   | 0.000 (2)    | -0.0034 (17) | -0.020 (2)   |
| F2B | 0.033 (2)   | 0.103 (4)   | 0.0269 (19) | -0.027 (3)   | 0.0100 (15)  | -0.006 (3)   |
| F3B | 0.075 (4)   | 0.059 (3)   | 0.085 (4)   | -0.002 (3)   | 0.026 (3)    | 0.021 (3)    |
| F4B | 0.038 (2)   | 0.091 (3)   | 0.0237 (17) | 0.009 (2)    | 0.0002 (14)  | -0.0136 (18) |
| O5B | 0.050 (3)   | 0.041 (2)   | 0.041 (2)   | -0.004 (2)   | -0.0052 (19) | 0.0051 (19)  |
| O5A | 0.040 (5)   | 0.037 (5)   | 0.030 (4)   | -0.001 (4)   | 0.000 (4)    | 0.002 (4)    |

*Geometric parameters (Å, °)*

|          |             |         |             |
|----------|-------------|---------|-------------|
| O4—C14   | 1.287 (2)   | C12—H12 | 0.9500      |
| O4—H1B   | 1.4248      | C7—C6   | 1.376 (2)   |
| O3—C14   | 1.2350 (19) | C7—H7   | 0.9500      |
| C14—C13  | 1.529 (2)   | C1—O2   | 1.2226 (19) |
| C13—N2   | 1.480 (2)   | C1—O1   | 1.2944 (19) |
| C13—H13  | 0.9900      | C1—C2   | 1.528 (2)   |
| C13—H13A | 0.9900      | C11—H11 | 0.9500      |
| N2—C10   | 1.349 (2)   | C6—H6   | 0.9500      |
| N2—C11   | 1.353 (2)   | C2—H2   | 0.9900      |
| C10—C9   | 1.384 (2)   | C2—H2A  | 0.9900      |
| C10—H10  | 0.9500      | F1A—B1A | 1.375 (5)   |
| C9—C8    | 1.398 (2)   | C4—C3   | 1.381 (2)   |
| C9—H9    | 0.9500      | C4—H4   | 0.9500      |
| C8—C12   | 1.399 (2)   | F2A—B1A | 1.370 (5)   |
| C8—C5    | 1.486 (2)   | C3—H3   | 0.9500      |
| C5—C4    | 1.396 (2)   | B1A—F4A | 1.384 (5)   |
| C5—C6    | 1.400 (2)   | B1A—F3A | 1.404 (6)   |
| N1—C3    | 1.348 (2)   | B1B—F2B | 1.364 (9)   |
| N1—C7    | 1.349 (2)   | B1B—F4B | 1.372 (12)  |
| N1—C2    | 1.479 (2)   | B1B—F1B | 1.380 (10)  |
| C12—C11  | 1.376 (2)   | B1B—F3B | 1.406 (11)  |

|                |              |                |              |
|----------------|--------------|----------------|--------------|
| C14—O4—H1B     | 109.7        | O2—C1—O1       | 126.19 (15)  |
| O3—C14—O4      | 126.40 (15)  | O2—C1—C2       | 121.66 (14)  |
| O3—C14—C13     | 116.20 (14)  | O1—C1—C2       | 112.15 (13)  |
| O4—C14—C13     | 117.40 (14)  | N2—C11—C12     | 120.56 (15)  |
| N2—C13—C14     | 113.73 (13)  | N2—C11—H11     | 119.7        |
| N2—C13—H13     | 108.8        | C12—C11—H11    | 119.7        |
| C14—C13—H13    | 108.8        | C7—C6—C5       | 120.26 (15)  |
| N2—C13—H13A    | 108.8        | C7—C6—H6       | 119.9        |
| C14—C13—H13A   | 108.8        | C5—C6—H6       | 119.9        |
| H13—C13—H13A   | 107.7        | N1—C2—C1       | 109.32 (13)  |
| C10—N2—C11     | 121.13 (14)  | N1—C2—H2       | 109.8        |
| C10—N2—C13     | 120.19 (13)  | C1—C2—H2       | 109.8        |
| C11—N2—C13     | 118.68 (13)  | N1—C2—H2A      | 109.8        |
| N2—C10—C9      | 120.27 (15)  | C1—C2—H2A      | 109.8        |
| N2—C10—H10     | 119.9        | H2—C2—H2A      | 108.3        |
| C9—C10—H10     | 119.9        | C3—C4—C5       | 119.62 (16)  |
| C10—C9—C8      | 119.83 (14)  | C3—C4—H4       | 120.2        |
| C10—C9—H9      | 120.1        | C5—C4—H4       | 120.2        |
| C8—C9—H9       | 120.1        | N1—C3—C4       | 120.75 (16)  |
| C9—C8—C12      | 118.34 (15)  | N1—C3—H3       | 119.6        |
| C9—C8—C5       | 121.34 (14)  | C4—C3—H3       | 119.6        |
| C12—C8—C5      | 120.25 (14)  | F2A—B1A—F1A    | 108.7 (4)    |
| C4—C5—C6       | 118.07 (15)  | F2A—B1A—F4A    | 108.8 (4)    |
| C4—C5—C8       | 121.48 (15)  | F1A—B1A—F4A    | 109.9 (4)    |
| C6—C5—C8       | 120.43 (15)  | F2A—B1A—F3A    | 109.0 (3)    |
| C3—N1—C7       | 121.07 (14)  | F1A—B1A—F3A    | 109.7 (4)    |
| C3—N1—C2       | 119.89 (14)  | F4A—B1A—F3A    | 110.7 (4)    |
| C7—N1—C2       | 118.82 (14)  | F2B—B1B—F4B    | 112.4 (7)    |
| C11—C12—C8     | 119.80 (15)  | F2B—B1B—F1B    | 111.9 (7)    |
| C11—C12—H12    | 120.1        | F4B—B1B—F1B    | 112.4 (7)    |
| C8—C12—H12     | 120.1        | F2B—B1B—F3B    | 108.5 (8)    |
| N1—C7—C6       | 120.23 (15)  | F4B—B1B—F3B    | 105.1 (7)    |
| N1—C7—H7       | 119.9        | F1B—B1B—F3B    | 106.0 (8)    |
| C6—C7—H7       | 119.9        |                |              |
| O3—C14—C13—N2  | 168.93 (14)  | C2—N1—C7—C6    | -174.36 (15) |
| O4—C14—C13—N2  | -11.5 (2)    | C10—N2—C11—C12 | -1.5 (2)     |
| C14—C13—N2—C10 | -107.12 (17) | C13—N2—C11—C12 | 178.25 (15)  |
| C14—C13—N2—C11 | 73.10 (19)   | C8—C12—C11—N2  | -0.8 (3)     |
| C11—N2—C10—C9  | 2.0 (2)      | N1—C7—C6—C5    | 0.6 (3)      |
| C13—N2—C10—C9  | -177.78 (15) | C4—C5—C6—C7    | -1.1 (2)     |
| N2—C10—C9—C8   | -0.2 (2)     | C8—C5—C6—C7    | 177.33 (15)  |
| C10—C9—C8—C12  | -2.0 (2)     | C3—N1—C2—C1    | -84.48 (19)  |
| C10—C9—C8—C5   | 175.02 (15)  | C7—N1—C2—C1    | 90.16 (17)   |
| C9—C8—C5—C4    | 30.3 (2)     | O2—C1—C2—N1    | 10.3 (2)     |
| C12—C8—C5—C4   | -152.72 (17) | O1—C1—C2—N1    | -169.22 (14) |
| C9—C8—C5—C6    | -148.12 (17) | C6—C5—C4—C3    | 0.9 (3)      |

|               |              |             |              |
|---------------|--------------|-------------|--------------|
| C12—C8—C5—C6  | 28.9 (2)     | C8—C5—C4—C3 | -177.53 (16) |
| C9—C8—C12—C11 | 2.5 (2)      | C7—N1—C3—C4 | -0.4 (3)     |
| C5—C8—C12—C11 | -174.60 (15) | C2—N1—C3—C4 | 174.09 (16)  |
| C3—N1—C7—C6   | 0.2 (3)      | C5—C4—C3—N1 | -0.1 (3)     |

*Hydrogen-bond geometry (Å, °)*

| <i>D</i> —H $\cdots$ <i>A</i>             | <i>D</i> —H | H $\cdots$ <i>A</i> | <i>D</i> $\cdots$ <i>A</i> | <i>D</i> —H $\cdots$ <i>A</i> |
|---|-------------|---------------------|----------------------------|-------------------------------|
| C13—H13 <i>A</i> $\cdots$ O1 <sup>i</sup> | 0.99        | 2.43                | 3.387 (2)                  | 161                           |
| C10—H10 $\cdots$ O3 <sup>ii</sup>         | 0.95        | 2.61                | 3.126 (2)                  | 114                           |
| C10—H10 $\cdots$ O1 <sup>i</sup>          | 0.95        | 2.51                | 3.362 (2)                  | 149                           |
| C12—H12 $\cdots$ O2 <sup>iii</sup>        | 0.95        | 2.28                | 3.188 (2)                  | 159                           |
| C7—H7 $\cdots$ O3 <sup>iv</sup>           | 0.95        | 2.34                | 3.208 (2)                  | 151                           |
| C2—H2 $\cdots$ O3 <sup>iv</sup>           | 0.99        | 2.36                | 3.231 (2)                  | 146                           |
| C4—H4 $\cdots$ O2 <sup>v</sup>            | 0.95        | 2.41                | 3.278 (2)                  | 151                           |
| O4—H1 <i>B</i> $\cdots$ O2 <sup>vi</sup>  | 1.42        | 2.39                | 3.3044 (17)                | 118.1                         |
| O1—H1 <i>B</i> $\cdots$ O4 <sup>vii</sup> | 1.05        | 1.42                | 2.4694 (18)                | 172.0                         |

Symmetry codes: (i)  $-x+3/2, y-1/2, -z+3/2$ ; (ii)  $-x, -y+1, -z+1$ ; (iii)  $x-1, y, z$ ; (iv)  $-x+1/2, y+1/2, -z+3/2$ ; (v)  $x-1/2, -y+3/2, z-1/2$ ; (vi)  $x-3/2, -y+3/2, z-1/2$ ; (vii)  $x-9/2, -y-7/2, z-7/2$ .