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## Structure Reports

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3,3'-Carbonyldipyridinium  
bis(perchlorate)

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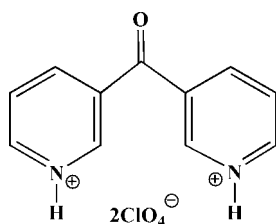
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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.028;  $wR$  factor = 0.073; data-to-parameter ratio = 11.6.

In the title molecular salt,  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}^{2+} \cdot 2\text{ClO}_4^-$ , the complete cation is generated by crystallographic twofold symmetry. The dihedral angle between the pyridyl rings is  $67.07(7)^\circ$ . The crystal structure features  $\text{N}-\text{H} \cdots \text{Cl}$  hydrogen bonds, forming sheets in the  $ab$  plane.

## Related literature

For the dipyrindyl ketone dication, see: Crook & McElvain (1930); Favaro *et al.* (1990). For metal complexes of di-3-pyridyl ketone, see: Chen & Mak (2005); Chen *et al.* (2009).



## Experimental

## Crystal data

 $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}^{2+} \cdot 2\text{ClO}_4^-$  $M_r = 385.11$ Orthorhombic,  $P2_12_12$  $a = 8.5315(3)$  Å $b = 15.1772(6)$  Å $c = 5.6107(2)$  Å $V = 726.50(5)$  Å<sup>3</sup> $Z = 2$ Mo  $K\alpha$  radiation  
 $\mu = 0.50$  mm<sup>-1</sup> $T = 296$  K  
 $0.40 \times 0.30 \times 0.20$  mm

## Data collection

Bruker APEXII CCD area-detector  
diffractometerAbsorption correction: multi-scan  
(*SADABS*; Bruker, 2007) $T_{\min} = 0.835$ ,  $T_{\max} = 0.905$ 6343 measured reflections  
1285 independent reflections  
1235 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.021$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.028$  $wR(F^2) = 0.073$  $S = 1.10$ 

1285 reflections

111 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.34$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -0.21$  e Å<sup>-3</sup>

Absolute structure: Flack (1983),

503 Friedel pairs

Flack parameter: 0.10 (10)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H7} \cdots \text{O2}$	0.86	2.22	2.907 (3)	136
$\text{N1}^i-\text{H7}^i \cdots \text{O4}$	0.86	2.34	2.967 (2)	130

Symmetry code: (i)  $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$ .

Data collection: *APEX2* (Bruker, 2007); cell refinement: *APEX2* and *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5923).

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## supporting information

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**3,3'-Carbonyldipyridinium bis(perchlorate)**

**Ya Zhang, Ai-min Li, Zhi-wei Wang and Chong-Qing Wan**

**S1. Comment**

Di-3-pyridyl ketone is an extraordinary ligand within the family of basic building blocks for construction of metal-organic complexes with intriguing architectures (Chen & Mak, 2005; Chen *et al.*, 2009). However, the crystal structure of salts with the dipyridyl ketone dication is rarely reported until now. Several related literatures discussed the relationship between the acid-base properties of the dipyridyl ketone isomers and the positions of the nitrogen atoms on the rings, which were investigated by spectrophotometric measurements (Crook & McElvain, 1930; Favaro *et al.*, 1990). In the present context, we report the structure of diprotonated di-3-pyridyl ketone perchlorate salt (Fig. 1). The two pyridyl rings exhibit a dihedral angle of 67.07 (7)°. The crystal structure is stabilized by N—H⋯(perchlorate) hydrogen bonds forming sheets in the *ab* plane.

**S2. Experimental**

Di-3-pyridyl ketone was prepared following the literature procedure of Chen & Mak (2005). Copper(II) perchlorate (37 mg, 0.1 mmol) was heated with di-3-pyridyl ketone (18 mg, 0.1 mmol) in acetonitrile (5 ml) at 373 K for 24 h. After cooling to room temperature, the precipitate which had formed was filtrated off. Crystals of the title salt was deposited by slow evaporation of the filtrate, which can be viewed as the product of the perchloric acid from the copper(II) perchlorate and di-3-pyridyl ketone (yield 11.5 mg, 30% based on di-3-pyridyl ketone).

**S3. Refinement**

H atoms were placed in idealized positions and allowed to ride on their parent atoms, with C—H = 0.93 Å and N—H = 0.86 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ .

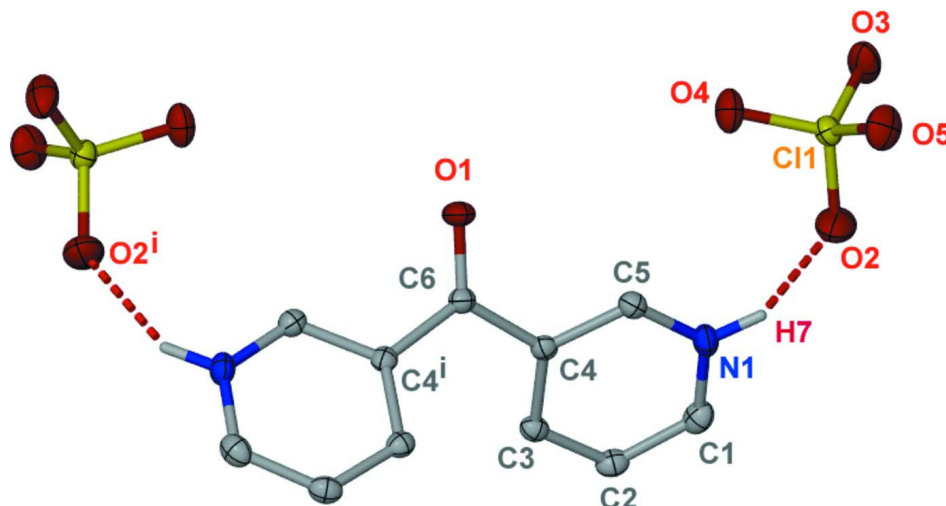


Figure 1

The atom-numbering scheme of the title salt; some H atoms have been omitted for clarity. Displacement ellipsoids are shown at the 30% probability level. [Symmetry code: (i)  $-x + 1, -y, z$ .]

### 3,3'-Carbonyldipyridinium diperchlorate

#### Crystal data

$C_{11}H_{10}N_2O^{2+} \cdot 2ClO_4^-$

$M_r = 385.11$

Orthorhombic,  $P2_12_12$

$a = 8.5315(3) \text{ \AA}$

$b = 15.1772(6) \text{ \AA}$

$c = 5.6107(2) \text{ \AA}$

$V = 726.50(5) \text{ \AA}^3$

$Z = 2$

$F(000) = 392$

$D_x = 1.760 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 256 reflections

$\theta = 2.3\text{--}26.2^\circ$

$\mu = 0.50 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Block, colorless

$0.40 \times 0.30 \times 0.20 \text{ mm}$

#### Data collection

Bruker APEXII CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2007)

$T_{\min} = 0.835, T_{\max} = 0.905$

6343 measured reflections

1285 independent reflections

1235 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 25.0^\circ, \theta_{\min} = 2.7^\circ$

$h = -10 \rightarrow 10$

$k = -18 \rightarrow 16$

$l = -6 \rightarrow 6$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.073$

$S = 1.10$

1285 reflections

111 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-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 0.4015P]$

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

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

$\Delta\rho_{\max} = 0.34 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.21 \text{ e \AA}^{-3}$

Extinction correction: *SHELXL97* (Sheldrick, 2008),  $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.019 (3)

Absolute structure: Flack (1983), 503 Friedel pairs  
 Absolute structure parameter: 0.10 (10)

*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 of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{iso}^*/U_{eq}$
C1	0.1257 (3)	0.13417 (17)	0.4051 (5)	0.0416 (6)
H1	0.0408	0.1642	0.3402	0.050*
C2	0.1807 (3)	0.05924 (17)	0.2988 (4)	0.0372 (6)
H2	0.1340	0.0381	0.1604	0.045*
C3	0.3062 (3)	0.01520 (14)	0.3985 (4)	0.0317 (5)
H3	0.3449	-0.0357	0.3274	0.038*
C4	0.3745 (3)	0.04756 (14)	0.6063 (4)	0.0287 (5)
C5	0.3158 (3)	0.12400 (15)	0.7048 (4)	0.0334 (5)
H5	0.3609	0.1474	0.8419	0.040*
C6	0.5000	0.0000	0.7390 (6)	0.0308 (7)
N1	0.1948 (2)	0.16399 (13)	0.6032 (4)	0.0386 (5)
H7	0.1591	0.2113	0.6677	0.046*
O1	0.5000	0.0000	0.9548 (4)	0.0431 (6)
Cl1	0.30796 (6)	0.32979 (4)	1.13244 (10)	0.03518 (19)
O2	0.2552 (3)	0.31908 (15)	0.8930 (4)	0.0720 (7)
O3	0.1779 (3)	0.33349 (15)	1.2909 (4)	0.0647 (6)
O4	0.4064 (2)	0.25628 (13)	1.1946 (4)	0.0539 (6)
O5	0.3940 (3)	0.41004 (13)	1.1460 (5)	0.0622 (6)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0318 (12)	0.0470 (14)	0.0461 (16)	0.0021 (11)	-0.0001 (12)	0.0095 (13)
C2	0.0350 (13)	0.0444 (14)	0.0323 (12)	-0.0082 (12)	-0.0038 (11)	0.0022 (10)
C3	0.0339 (11)	0.0321 (12)	0.0293 (11)	-0.0041 (10)	0.0037 (12)	-0.0010 (10)
C4	0.0293 (11)	0.0299 (11)	0.0269 (11)	-0.0019 (9)	0.0043 (11)	0.0025 (10)
C5	0.0348 (12)	0.0336 (12)	0.0319 (12)	-0.0013 (11)	0.0021 (11)	-0.0022 (9)
C6	0.0346 (18)	0.0289 (17)	0.0288 (18)	-0.0017 (15)	0.000	0.000
N1	0.0378 (10)	0.0327 (10)	0.0452 (12)	0.0081 (10)	0.0046 (10)	-0.0007 (10)
O1	0.0499 (15)	0.0537 (16)	0.0259 (13)	0.0073 (14)	0.000	0.000
Cl1	0.0335 (3)	0.0328 (3)	0.0393 (3)	-0.0005 (2)	0.0001 (3)	-0.0034 (3)
O2	0.0990 (17)	0.0660 (14)	0.0511 (12)	0.0026 (13)	-0.0214 (12)	-0.0129 (12)

O3	0.0620 (13)	0.0551 (12)	0.0770 (15)	0.0139 (12)	0.0314 (11)	0.0109 (12)
O4	0.0398 (10)	0.0402 (10)	0.0817 (16)	0.0070 (8)	-0.0062 (10)	-0.0008 (10)
O5	0.0604 (12)	0.0403 (11)	0.0858 (16)	-0.0138 (9)	-0.0075 (14)	0.0029 (12)

*Geometric parameters (Å, °)*

C1—N1	1.337 (3)	C5—N1	1.327 (3)
C1—C2	1.368 (4)	C5—H5	0.9300
C1—H1	0.9300	C6—O1	1.210 (4)
C2—C3	1.381 (4)	C6—C4 <sup>i</sup>	1.491 (3)
C2—H2	0.9300	N1—H7	0.8600
C3—C4	1.393 (3)	C11—O3	1.423 (2)
C3—H3	0.9300	C11—O5	1.4242 (19)
C4—C5	1.379 (3)	C11—O2	1.426 (2)
C4—C6	1.491 (3)	C11—O4	1.439 (2)
N1—C1—C2	119.5 (2)	C4—C5—H5	120.2
N1—C1—H1	120.2	O1—C6—C4	119.97 (14)
C2—C1—H1	120.2	O1—C6—C4 <sup>i</sup>	119.97 (14)
C1—C2—C3	119.5 (2)	C4—C6—C4 <sup>i</sup>	120.1 (3)
C1—C2—H2	120.3	C5—N1—C1	123.1 (2)
C3—C2—H2	120.3	C5—N1—H7	118.5
C2—C3—C4	119.5 (2)	C1—N1—H7	118.5
C2—C3—H3	120.2	O3—C11—O5	109.56 (14)
C4—C3—H3	120.2	O3—C11—O2	110.31 (16)
C5—C4—C3	118.7 (2)	O5—C11—O2	108.08 (15)
C5—C4—C6	117.9 (2)	O3—C11—O4	109.53 (13)
C3—C4—C6	123.2 (2)	O5—C11—O4	110.44 (12)
N1—C5—C4	119.7 (2)	O2—C11—O4	108.90 (14)
N1—C5—H5	120.2		
N1—C1—C2—C3	0.4 (4)	C5—C4—C6—O1	34.0 (2)
C1—C2—C3—C4	0.2 (3)	C3—C4—C6—O1	-141.03 (17)
C2—C3—C4—C5	-1.0 (3)	C5—C4—C6—C4 <sup>i</sup>	-146.0 (2)
C2—C3—C4—C6	174.0 (2)	C3—C4—C6—C4 <sup>i</sup>	38.97 (17)
C3—C4—C5—N1	1.2 (3)	C4—C5—N1—C1	-0.6 (4)
C6—C4—C5—N1	-174.1 (2)	C2—C1—N1—C5	-0.2 (4)

Symmetry code: (i)  $-x+1, -y, z$ .*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>
N1—H7 $\cdots$ O2	0.86	2.22	2.907 (3)	136
N1 <sup>ii</sup> —H7 <sup>ii</sup> $\cdots$ O4	0.86	2.34	2.967 (2)	130

Symmetry code: (ii)  $x+1/2, -y+1/2, -z+2$ .