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## Structure Reports

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## 1,10-Phenanthroline-5,6-dione ethanol monosolvate

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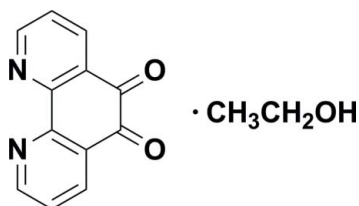
Received 30 March 2014; accepted 11 April 2014

Key indicators: single-crystal X-ray study;  $T = 123$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.040;  $wR$  factor = 0.114; data-to-parameter ratio = 12.2.

In the title compound,  $\text{C}_{12}\text{H}_6\text{N}_2\text{O}_2 \cdot \text{C}_2\text{H}_5\text{OH}$ , the molecule of the 1,10-phenanthroline-5,6-dione is approximately planar, with a maximum deviation of 0.051 (1) Å. In the crystal, molecules are linked by  $\text{O}-\text{H} \cdots \text{N}$  and weak  $\text{C}-\text{H} \cdots \text{O}$  hydrogen bonds, forming supramolecular chains propagating along [110].  $\pi-\pi$  stacking interactions are observed between the pyridine rings of neighbouring chains, the centroid-centroid separations being 3.6226 (11) and 3.7543 (11) Å.

## Related literature

For background to and applications of 1,10-phenanthroline-5,6-dione, see: Smith & Cagle (1947); Ma *et al.* (2010); Goss & Abruna (1985); Murphy *et al.* (2011); Wu *et al.* (1996); Pinczewska *et al.* (2012); Poteet & MacDonnell (2013); Wu *et al.* (2002); Poteet *et al.* (2013); Paw *et al.* (1998). For the synthesis, see: Paw & Eisenberg (1997). For a related structure, see: Calderazzo *et al.* (1999).



## Experimental

## Crystal data

 $\text{C}_{12}\text{H}_6\text{N}_2\text{O}_2 \cdot \text{C}_2\text{H}_6\text{O}$  $M_r = 256.26$ Triclinic,  $P\bar{1}$  $a = 7.3064$  (15) Å $b = 9.1055$  (18) Å $c = 9.7291$  (19) Å $\alpha = 96.47$  (3)° $\beta = 101.68$  (3)° $\gamma = 109.83$  (3)° $V = 584.6$  (2) Å<sup>3</sup> $Z = 2$ Mo  $K\alpha$  radiation $\mu = 0.10$  mm<sup>-1</sup> $T = 123$  K

0.20 × 0.20 × 0.20 mm

## Data collection

Rigaku Saturn724+ diffractometer

5059 measured reflections

2252 independent reflections

2074 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.020$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.040$  $wR(F^2) = 0.114$  $S = 1.06$ 

2252 reflections

185 parameters

1 restraint

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.24$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -0.17$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O3}-\text{H3O} \cdots \text{N1}^{\text{i}}$	0.85 (1)	2.08 (1)	2.8258 (19)	146 (2)
$\text{C1}-\text{H1} \cdots \text{O2}^{\text{ii}}$	0.95	2.53	3.3381 (19)	143

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

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: XU5783).

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## supporting information

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## 1,10-Phenanthroline-5,6-dione ethanol monosolvate

Jing-Wei Dai, Zhao-Yang Li and Osamu Sato

### S1. Experimental

#### S1.1. Synthesis and crystallization

The title compound was prepared according to literature method (Paw & Eisenberg, 1997). An ice-cold mixture of concentrated H<sub>2</sub>SO<sub>4</sub> (40 mL) and HNO<sub>3</sub> (20 mL) was added to 4 g of 1,10-phenanthroline (0.02 mol) and 4 g of KBr (0.03 mol). The mixture was heated at 90 °C for 3 h. The hot yellow solution was poured over 200 mL of ice and neutralized carefully with sodium hydroxide until neutral to slightly acidic pH. Extraction with CH<sub>2</sub>Cl<sub>2</sub> (4\*100 mL) followed by drying with Na<sub>2</sub>SO<sub>4</sub> and removal of solvent gave 2.8 g (yield = 67%) of 1,10-phenanthroline-5,6-dione. This product was purified further by crystallization from ethanol.

#### S1.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Carbon-bound H-atoms were placed in calculated positions and were included in the refinement in the riding model approximation with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms and  $1.2U_{\text{eq}}(\text{C})$  for the others. The hydroxy H atom was located in a difference Fourier map, and was refined with distance restraints of  $\text{O}-\text{H} = 0.84 \pm 0.01$ ,  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ .

### S2. Results and discussion

1,10-Phenanthroline-5,6-dione has been known for many years (Smith & Cagle, 1947), and its chelating ability as either a diimine or a catecholate was important in coordination chemistry (Ma *et al.*, 2010, Goss & Abruna, 1985, Murphy *et al.*, 2011), analytical chemistry (Wu *et al.*, 1996, Pinczewska *et al.*, 2012) and biophysical chemistry (Poteet & MacDonnell, 2013, Wu *et al.*, 2002, Poteet *et al.*, 2013). Moreover, it can become as the bridging ligand, which has shown very interesting function in multinuclear complexes (Paw *et al.*, 1998, Paw & Eisenberg, 1997, Calderazzo *et al.*, 1999).

According to the structural analysis, the bond lengths and angles of the title compound are generally within normal ranges. The asymmetric unit of the title compound consists of one 1,10-phenanthroline-5,6-dione molecule and one ethanol molecule. Between molecules, O—H $\cdots$ N and C—H $\cdots$ O hydrogen bonds can be found that further form one-dimensional chain. The weak  $\pi\cdots\pi$  stacking interactions between adjacent chains are also observed [centroid–centroid separations being 3.6226 (11) and 3.7543 (11) Å].

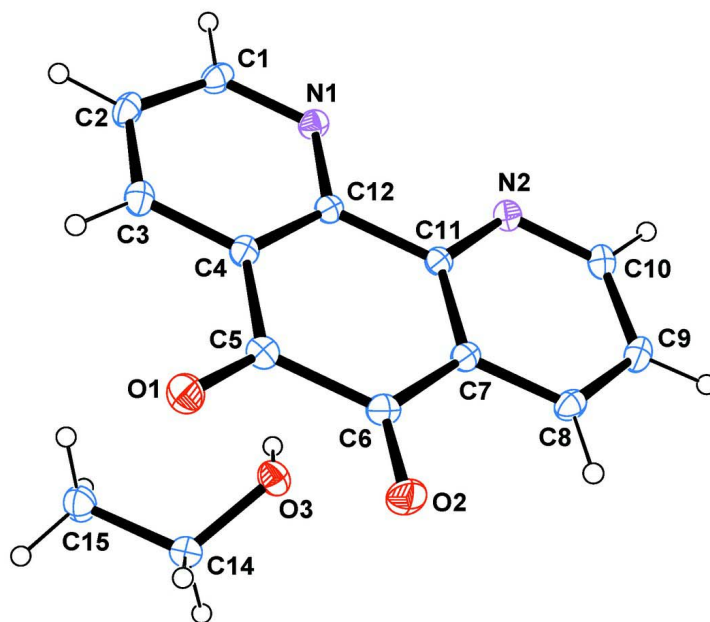


Figure 1

Crystal structure of the title compound with labeling and displacement ellipsoids drawn at the 30% probability level.

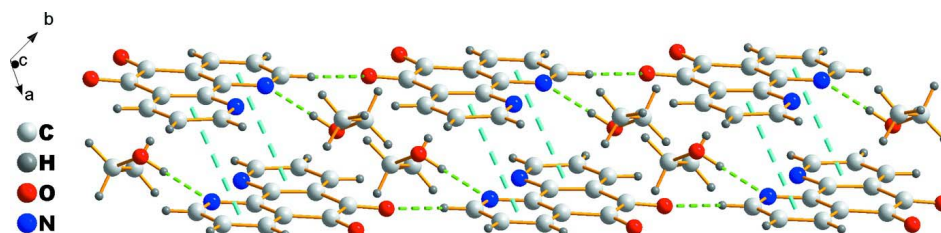


Figure 2

Crystal packing of the title compound. Intermolecular O—H...N and C—H...O hydrogen bonds are shown as green dashed lines, and  $\pi$ - $\pi$  stacking interactions between molecules are shown as blue dashed lines.

### 1,10-Phenanthroline-5,6-dione ethanol monosolvate

#### Crystal data

$C_{12}H_6N_2O_2 \cdot C_2H_6O$

$M_r = 256.26$

Triclinic,  $P\bar{1}$

Hall symbol: -P 1

$a = 7.3064$  (15) Å

$b = 9.1055$  (18) Å

$c = 9.7291$  (19) Å

$\alpha = 96.47$  (3)°

$\beta = 101.68$  (3)°

$\gamma = 109.83$  (3)°

$V = 584.6$  (2) Å<sup>3</sup>

$Z = 2$

$F(000) = 268$

$D_x = 1.456$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2355 reflections

$\theta = 3.1$ – $30.2$ °

$\mu = 0.10$  mm<sup>-1</sup>

$T = 123$  K

Block, yellow

$0.20 \times 0.20 \times 0.20$  mm

Data collection

Rigaku Saturn724+  
diffractometer  
Radiation source: Rotating Anode  
Confocal monochromator  
Detector resolution: 28.5714 pixels mm<sup>-1</sup>  
 $\omega$  scans  
5059 measured reflections

2252 independent reflections  
2074 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.020$   
 $\theta_{\text{max}} = 26.0^\circ$ ,  $\theta_{\text{min}} = 3.1^\circ$   
 $h = -9 \rightarrow 9$   
 $k = -11 \rightarrow 11$   
 $l = -11 \rightarrow 11$

Refinement

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.114$   
 $S = 1.06$   
2252 reflections  
185 parameters  
1 restraint  
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  
 $w = 1/[\sigma^2(F_o^2) + (0.0709P)^2 + 0.118P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.24 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.17 \text{ e } \text{Å}^{-3}$

Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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  $F^2 > \sigma(F^2)$  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 ( $\text{Å}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C4	0.66468 (17)	0.96363 (14)	0.27101 (12)	0.0211 (3)
C11	0.69855 (17)	0.93910 (13)	0.52865 (12)	0.0196 (3)
C5	0.50156 (18)	0.80403 (14)	0.22423 (12)	0.0237 (3)
C7	0.54977 (17)	0.78514 (14)	0.49173 (12)	0.0211 (3)
C6	0.43997 (17)	0.70995 (13)	0.34035 (13)	0.0239 (3)
C12	0.75757 (16)	1.02974 (13)	0.41609 (12)	0.0200 (3)
C8	0.50365 (18)	0.70329 (14)	0.60099 (13)	0.0250 (3)
H8	0.4042	0.5987	0.5794	0.030*
C9	0.60544 (18)	0.77748 (15)	0.74108 (13)	0.0270 (3)
H9	0.5787	0.7248	0.8179	0.032*
C3	0.72616 (18)	1.05260 (15)	0.16952 (13)	0.0252 (3)
H3	0.6651	1.0108	0.0704	0.030*
C1	0.95979 (18)	1.25750 (14)	0.36088 (14)	0.0262 (3)
H1	1.0632	1.3603	0.3919	0.031*
C10	0.74812 (18)	0.93131 (15)	0.76688 (13)	0.0261 (3)
H10	0.8166	0.9818	0.8636	0.031*
C2	0.87625 (19)	1.20164 (15)	0.21448 (14)	0.0272 (3)

H2	0.9213	1.2644	0.1475	0.033*
O1	0.41332 (14)	0.74720 (11)	0.09901 (9)	0.0331 (3)
O2	0.30275 (14)	0.58111 (10)	0.30567 (10)	0.0333 (3)
N2	0.79532 (15)	1.01274 (12)	0.66490 (10)	0.0237 (2)
N1	0.90359 (15)	1.17542 (12)	0.46054 (11)	0.0233 (2)
C15	0.8686 (2)	0.65765 (16)	0.07549 (14)	0.0336 (3)
H15A	0.8325	0.7503	0.0621	0.050*
H15B	0.8372	0.5885	-0.0177	0.050*
H15C	1.0130	0.6934	0.1211	0.050*
C14	0.7508 (2)	0.56671 (15)	0.16901 (14)	0.0312 (3)
O3	0.76490 (13)	0.66129 (10)	0.30034 (9)	0.0291 (2)
H14A	0.598 (3)	0.5214 (19)	0.1167 (17)	0.042 (4)*
H14B	0.797 (3)	0.479 (2)	0.1910 (18)	0.048 (5)*
H3O	0.8864 (17)	0.719 (2)	0.3431 (19)	0.058 (5)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C4	0.0190 (6)	0.0245 (6)	0.0236 (6)	0.0108 (5)	0.0073 (4)	0.0073 (5)
C11	0.0173 (5)	0.0214 (6)	0.0226 (6)	0.0091 (4)	0.0069 (4)	0.0051 (4)
C5	0.0215 (6)	0.0259 (6)	0.0238 (6)	0.0102 (5)	0.0044 (5)	0.0036 (5)
C7	0.0188 (6)	0.0219 (6)	0.0252 (6)	0.0091 (5)	0.0077 (4)	0.0064 (4)
C6	0.0205 (6)	0.0222 (6)	0.0291 (6)	0.0078 (5)	0.0068 (5)	0.0043 (5)
C12	0.0168 (5)	0.0216 (6)	0.0238 (6)	0.0086 (4)	0.0070 (4)	0.0053 (4)
C8	0.0217 (6)	0.0231 (6)	0.0330 (7)	0.0085 (5)	0.0107 (5)	0.0100 (5)
C9	0.0266 (6)	0.0333 (7)	0.0277 (6)	0.0138 (5)	0.0118 (5)	0.0145 (5)
C3	0.0242 (6)	0.0326 (7)	0.0240 (6)	0.0143 (5)	0.0085 (5)	0.0095 (5)
C1	0.0215 (6)	0.0234 (6)	0.0355 (7)	0.0065 (5)	0.0113 (5)	0.0107 (5)
C10	0.0260 (6)	0.0332 (7)	0.0215 (6)	0.0124 (5)	0.0077 (5)	0.0069 (5)
C2	0.0268 (6)	0.0324 (7)	0.0318 (7)	0.0150 (5)	0.0157 (5)	0.0163 (5)
O1	0.0338 (5)	0.0333 (5)	0.0238 (5)	0.0072 (4)	0.0005 (4)	0.0019 (4)
O2	0.0290 (5)	0.0249 (5)	0.0346 (5)	-0.0012 (4)	0.0051 (4)	0.0027 (4)
N2	0.0234 (5)	0.0257 (5)	0.0222 (5)	0.0088 (4)	0.0070 (4)	0.0044 (4)
N1	0.0200 (5)	0.0223 (5)	0.0276 (5)	0.0068 (4)	0.0076 (4)	0.0060 (4)
C15	0.0321 (7)	0.0332 (7)	0.0282 (7)	0.0040 (5)	0.0083 (5)	0.0019 (5)
C14	0.0388 (8)	0.0250 (6)	0.0296 (7)	0.0104 (5)	0.0116 (6)	0.0043 (5)
O3	0.0255 (5)	0.0329 (5)	0.0261 (5)	0.0092 (4)	0.0059 (4)	0.0007 (4)

*Geometric parameters (Å, °)*

C4—C3	1.3950 (17)	C3—C2	1.3776 (19)
C4—C12	1.3995 (17)	C3—H3	0.9500
C4—C5	1.4818 (18)	C1—N1	1.3355 (16)
C11—N2	1.3436 (16)	C1—C2	1.3907 (18)
C11—C7	1.4037 (17)	C1—H1	0.9500
C11—C12	1.4899 (16)	C10—N2	1.3357 (16)
C5—O1	1.2171 (15)	C10—H10	0.9500
C5—C6	1.5411 (17)	C2—H2	0.9500

C7—C8	1.3972 (17)	C15—C14	1.5026 (18)
C7—C6	1.4843 (18)	C15—H15A	0.9800
C6—O2	1.2128 (16)	C15—H15B	0.9800
C12—N1	1.3448 (16)	C15—H15C	0.9800
C8—C9	1.3813 (18)	C14—O3	1.4225 (15)
C8—H8	0.9500	C14—H14A	1.040 (18)
C9—C10	1.3914 (19)	C14—H14B	0.995 (18)
C9—H9	0.9500	O3—H3O	0.850 (10)
C3—C4—C12	118.58 (11)	C4—C3—H3	120.3
C3—C4—C5	119.93 (11)	N1—C1—C2	124.01 (11)
C12—C4—C5	121.48 (11)	N1—C1—H1	118.0
N2—C11—C7	122.79 (11)	C2—C1—H1	118.0
N2—C11—C12	116.36 (10)	N2—C10—C9	124.42 (12)
C7—C11—C12	120.85 (11)	N2—C10—H10	117.8
O1—C5—C4	122.47 (12)	C9—C10—H10	117.8
O1—C5—C6	119.54 (11)	C3—C2—C1	117.99 (11)
C4—C5—C6	117.97 (10)	C3—C2—H2	121.0
C8—C7—C11	118.69 (11)	C1—C2—H2	121.0
C8—C7—C6	119.96 (11)	C10—N2—C11	117.08 (11)
C11—C7—C6	121.35 (11)	C1—N1—C12	117.77 (11)
O2—C6—C7	122.90 (12)	C14—C15—H15A	109.5
O2—C6—C5	119.48 (11)	C14—C15—H15B	109.5
C7—C6—C5	117.60 (10)	H15A—C15—H15B	109.5
N1—C12—C4	122.28 (11)	C14—C15—H15C	109.5
N1—C12—C11	117.04 (10)	H15A—C15—H15C	109.5
C4—C12—C11	120.68 (11)	H15B—C15—H15C	109.5
C9—C8—C7	118.69 (11)	O3—C14—C15	114.19 (11)
C9—C8—H8	120.7	O3—C14—H14A	104.6 (9)
C7—C8—H8	120.7	C15—C14—H14A	109.3 (9)
C8—C9—C10	118.31 (11)	O3—C14—H14B	108.5 (10)
C8—C9—H9	120.8	C15—C14—H14B	109.8 (10)
C10—C9—H9	120.8	H14A—C14—H14B	110.5 (14)
C2—C3—C4	119.37 (12)	C14—O3—H3O	111.5 (14)
C2—C3—H3	120.3		

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3O $\cdots$ N1 <sup>i</sup>	0.85 (1)	2.08 (1)	2.8258 (19)	146 (2)
C1—H1 $\cdots$ O2 <sup>ii</sup>	0.95	2.53	3.3381 (19)	143

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