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

Jing-Wei Dai,[a] Zhao-Yang Li[b] and Osamu Sato[a]*

[a]Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan, and [b]Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki-Aza-Aoba, Aoba-ku, Sendai 980-8578, Japan
Correspondence e-mail: sato@cm.kyushu-u.ac.jp

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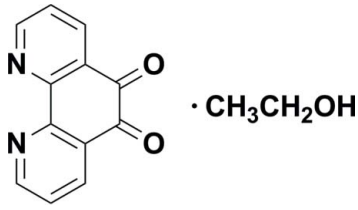
Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.002 Å; R factor = 0.040; wR factor = 0.114; data-to-parameter ratio = 12.2.

In the title compound, $C_{12}H_6N_2O_2\cdot C_2H_5OH$, 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 O—H···N and weak C—H···O hydrogen bonds, forming supramolecular chains propagating along [110]. π–π 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

$C_{12}H_6N_2O_2\cdot C_2H_6O$
M_r = 256.26
Triclinic, $P\overline{1}$
a = 7.3064 (15) Å
b = 9.1055 (18) Å
c = 9.7291 (19) Å
α = 96.47 (3)°
β = 101.68 (3)°
γ = 109.83 (3)°
V = 584.6 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
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_{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
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3O···N1^{i}	0.85 (1)	2.08 (1)	2.8258 (19)	146 (2)
C1—H1···O2^{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: *publCIF* (Westrip, 2010).

The authors would like to thank the China Scholarship Council (CSC).

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

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supplementary materials

Acta Cryst. (2014). E**70**, o573 [doi:10.1107/S1600536814008241]

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

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

1. Introduction

2. Experimental

2.1. Synthesis and crystallization

The title compound was prepared according to literature method (Paw & Eisenberg, 1997). An ice-cold mixture of concentrated H_2SO_4 (40 mL) and HNO_3 (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 ºC 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_2Cl_2 (4*100 mL) followed by drying with Na_2SO_4 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.

2.2. 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 $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for the others. The hydroxy H atom was located in a difference Fourier map, and was refined with distance restraints of O—H = 0.84±0.01, $U_{iso}(H) = 1.2U_{eq}(O)$.

3. 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···N and C—H···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].

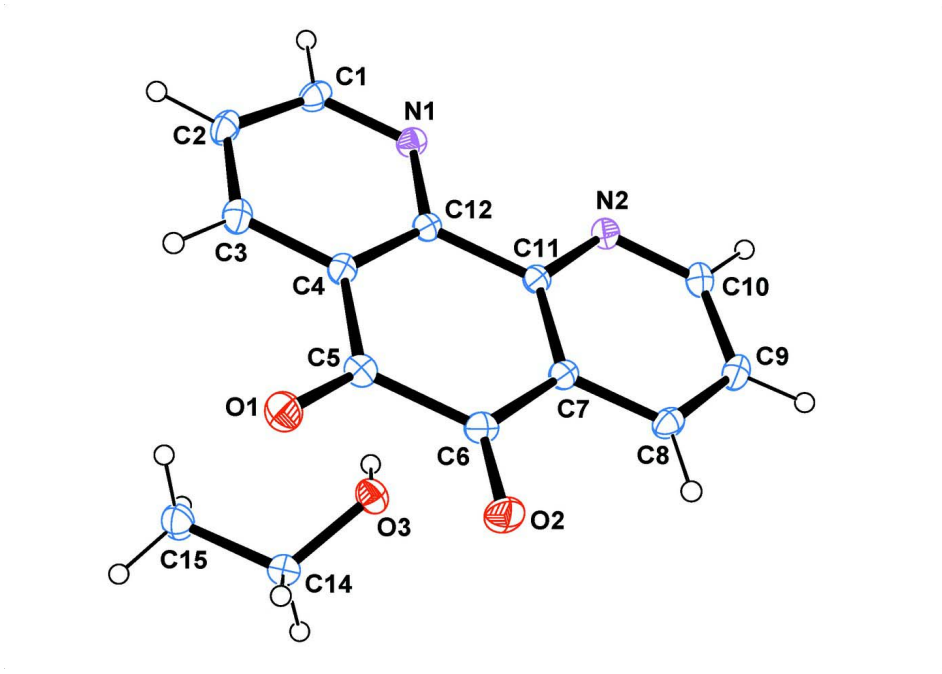

Figure 1

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

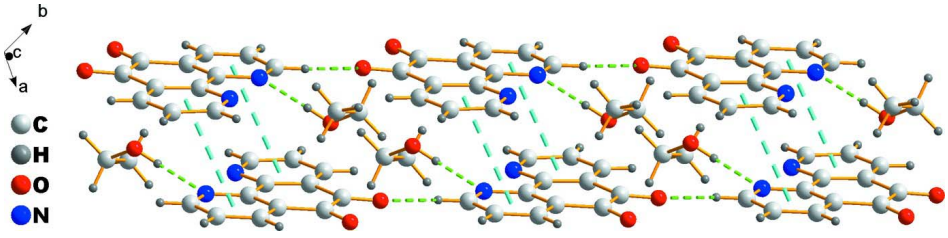

Figure 2

Crystal packing of the title compound. Intermolecular O—H···N and C—H···O hydrogen bonds are shown as green dashed lines, and π-π 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, $P\overline{1}$
Hall symbol: -P 1
a = 7.3064 (15) Å
b = 9.1055 (18) Å
c = 9.7291 (19) Å
α = 96.47 (3)°
β = 101.68 (3)°
γ = 109.83 (3)°
V = 584.6 (2) Å^3

Z = 2
$F(000)$ = 268
D_x = 1.456 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2355 reflections
θ = 3.1–30.2°
μ = 0.10 mm^{-1}
T = 123 K
Block, yellow
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku Saturn724+ diffractometer
Radiation source: Rotating Anode
Confocal monochromator
Detector resolution: 28.5714 pixels mm^{-1}
ω scans
5059 measured reflections
2252 independent reflections
2074 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 26.0°$, $\theta_{min} = 3.1°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 11$

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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e 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 (Å^2)

	x	y	z	U_{iso}*/U_{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 (Å²)

	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, º)

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 (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*O*···N1^{i}	0.85 (1)	2.08 (1)	2.8258 (19)	146 (2)
C1—H1···O2^{ii}	0.95	2.53	3.3381 (19)	143

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