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2-Phenylimidazo[4,5-*f*][1,10]phenanthroline-1,10-diium dichloride dihydrate

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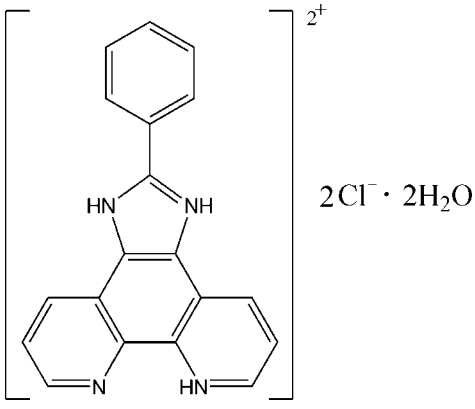
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.003 Å; R factor = 0.043; wR factor = 0.140; data-to-parameter ratio = 16.4.

The title salt, $C_{19}H_{14}N_4^{2+}\cdot 2Cl^-\cdot 2H_2O$, features π–π stacking of the cations (centroid–centroid distance = 3.69 Å). The benzene ring deviates slightly from the imidazo[4,5-*f*]1,10-phenanthroline plane, making a dihedral angle of 10.66 (11)°. N—H···O, N—H···Cl and O—H···Cl hydrogen bonds along with π–π stacking interactions link the cations, anions and water molecules into a three-dimensional supramolecular network.

Related literature

For the synthesis of (2-phenyl)-imidazo[4,5-*f*]1,10-phenanthroline, see: Li *et al.* (2001). For background, see Zhou *et al.*(2005).



Experimental

Crystal data

$C_{19}H_{14}N_4^{2+}\cdot 2Cl^-\cdot 2H_2O$
M_r = 405.27
Triclinic, $P\overline{1}$
a = 9.1296 (18) Å
b = 9.4443 (19) Å
c = 11.570 (2) Å
α = 100.77 (3)°
β = 107.28 (3)°
γ = 97.99 (3)°
V = 915.4 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.38 mm^{-1}
T = 291 (2) K
0.41 × 0.33 × 0.13 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.862, T_{max} = 0.954
9050 measured reflections
4148 independent reflections
3097 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.140
S = 1.02
4148 reflections
253 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H7···Cl1^{i}	0.846 (10)	2.266 (15)	3.0187 (19)	148 (2)
N3—H9···O1^{ii}	0.849 (10)	1.878 (11)	2.719 (2)	171 (2)
N4—H8···Cl2	0.848 (10)	2.233 (10)	3.078 (2)	175 (2)
O1—H15···O2^{i}	0.85	1.90	2.748 (3)	173
O1—H16···Cl2^{iii}	0.85	2.29	3.110 (2)	163
O2—H17···Cl1	0.85	2.37	3.194 (3)	164
O2—H18···Cl2	0.85	2.38	3.204 (2)	162

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2372).

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supplementary materials

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2-Phenylimidazo[4,5-*f*][1,10]phenanthroline-1,10-diium dichloride dihydrate

Y.-H. Yu, Y. Su, A.-E. Shi and G.-F. Hou

Comment

The (2-phenyl)-imidazo[4,5-*f*]1,10-phenanthroline is a conjugated plane molecule which is studied as photochemistry material (Li *et al.*., 2001; Zhou *et al.*., 2005). In our attempt to synthesize the europium complex with the (2-phenyl)-imidazo[4,5-*f*]1,10-phenanthroline molecule, we unexpectedly obtained the title compound (I). Herein, we report its crystal structure.

In the cation of (I) (Figure 1), the benzene ring is slightly deviate from imidazo[4,5-*f*]1,10-phenanthroline plane, with the dihedral angles between the two planes are 10.66 (0.11) °, which is agreement with similary structure reported values (Zhou *et al.*, 2005). The π-π stacking interactions between the cation components is observed, with the distance between the π-π stacking planes are 3.69 Å.

In the crystal structure, the cations and anions are linked by N—H···Cl hydrogen bonds. In addition, the water molecules are both as acceptor and donor of hydrogen bond link these molecule into a three dimensional supramolecular network *via* N—H···O, O—H···Cl hydrogen bonds (Table 1; Figure 2).

Experimental

(2-phenyl)-imidazo[4,5-*f*]1,10-phenanthroline was prepared of 1,10-phenanthroline, ammonium acetate and benzaldehyde in acetic acid solution (Li *et al.*, 2001). Europium trinitrate (0.834 g, 1 mmol) and (2-phenyl)-imidazo[4,5-*f*]1,10-phenanthroline (0.296 g, 1 mmol) were dissolved in hot methanol solution (15 ml) and added two drops hydrochloric acid then a clear solution was obtained. The resulting solution was allowed to stand in a desiccator at room temperature for several days. Yellow crystals of (I) were obtained. Unexpectedly, the salt-type adducts of this ligands was crystallized from solution.

Refinement

H atoms bound to C atoms were placed in calculated positions and treated as riding on their parent atoms, with C—H = 0.93 Å (Caromatic) and with U_{iso}(H) = 1.2U_{eq}(C). The N-bound H atoms were located in a difference Fourier map and restrained refined, with N—H = 0.85 Å, U_{iso}(H) = 1.2U_{eq}(N). Water H atoms were initially located in a difference Fourier map but they were treated as riding on their parent atoms with O—H = 0.85 Å, H···H = 1.39 and with U_{iso}(H) = 1.5U_{eq}(O).

Figures

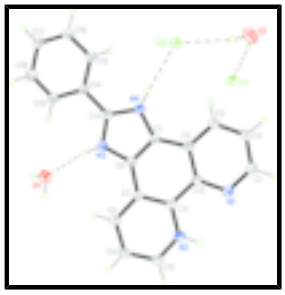

Fig. 1. The molecular structure of (I), showing displacement ellipsoids at the 30% probability level for non-H atoms. Dashed lines indicate the intramolecular hydrogen bonding interactions.

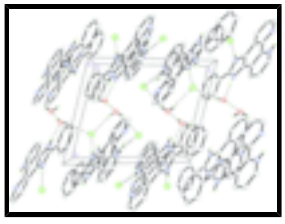

Fig. 2. A partial packing view, showing the three-dimensional hydrogen-bonding network. Dashed lines indicate the hydrogen-bonding interactions. H atoms not involved in hydrogen bonds have been omitted.

2-Phenylimidazo[4,5-*f*][1,10]phenanthroline-1,10-diium dichloride dihydrate

Crystal data

$C_{19}H_{14}N_4^{2+}\cdot 2Cl^-\cdot 2H_2O$	$Z = 2$
$M_r = 405.27$	$F_{000} = 420$
Triclinic, $P\overline{1}$	$D_x = 1.470$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 9.1296$ (18) Å	Cell parameters from 7394 reflections
$b = 9.4443$ (19) Å	$\theta = 3.3$–27.5°
$c = 11.570$ (2) Å	$\mu = 0.38$ mm^{-1}
$\alpha = 100.77$ (3)°	$T = 291$ (2) K
$\beta = 107.28$ (3)°	Block, yellow
$\gamma = 97.99$ (3)°	0.41 × 0.33 × 0.13 mm
$V = 915.4$ (3) Å^3	

Data collection

Rigaku RAXIS-RAPID diffractometer	4148 independent reflections
Radiation source: fine-focus sealed tube	3097 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.023$
$T = 291(2)$ K	$\theta_{max} = 27.5^\circ$
ω scan	$\theta_{min} = 3.3^\circ$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$h = -11\rightarrow11$
$T_{min} = 0.862$, $T_{max} = 0.954$	$k = -12\rightarrow12$
9050 measured reflections	$l = -14\rightarrow15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.043$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.140$	$w = 1/[\sigma^2(F_o^2) + (0.0945P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
4148 reflections	$\Delta\rho_{max} = 0.42$ e Å^{-3}
253 parameters	$\Delta\rho_{min} = -0.39$ e Å^{-3}
3 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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 $F^2 > 2$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}
C1	0.8174 (3)	0.5897 (2)	0.4089 (2)	0.0438 (5)
H1	0.8518	0.5134	0.4425	0.053*
C2	0.6570 (2)	0.5846 (2)	0.3663 (2)	0.0442 (5)
H2	0.5873	0.5080	0.3739	0.053*
C3	0.6021 (2)	0.6933 (2)	0.3132 (2)	0.0405 (5)
H3	0.4952	0.6916	0.2841	0.049*
C4	0.7100 (2)	0.8064 (2)	0.30349 (18)	0.0319 (4)
C5	0.6739 (2)	0.9294 (2)	0.25259 (18)	0.0308 (4)
C6	0.7855 (2)	1.0413 (2)	0.25277 (18)	0.0308 (4)
C7	0.9497 (2)	1.0438 (2)	0.30065 (17)	0.0307 (4)
C8	1.0694 (2)	1.1530 (2)	0.3015 (2)	0.0379 (5)
H4	1.0451	1.2330	0.2689	0.045*
C9	1.2244 (2)	1.1430 (3)	0.3504 (2)	0.0421 (5)
H5	1.3052	1.2155	0.3514	0.050*
C10	1.2557 (2)	1.0232 (3)	0.3976 (2)	0.0405 (5)
H6	1.3594	1.0150	0.4312	0.049*

C11	0.9877 (2)	0.9229 (2)	0.34916 (17)	0.0303 (4)
C12	0.8708 (2)	0.8041 (2)	0.35256 (18)	0.0314 (4)
C13	0.5554 (2)	1.0910 (2)	0.16524 (18)	0.0312 (4)
C14	0.4330 (2)	1.1638 (2)	0.10563 (18)	0.0318 (4)
C15	0.2758 (2)	1.0932 (2)	0.0612 (2)	0.0394 (5)
H10	0.2472	0.9975	0.0679	0.047*
C16	0.1624 (2)	1.1657 (3)	0.0071 (2)	0.0440 (5)
H11	0.0576	1.1179	−0.0222	0.053*
C17	0.2012 (2)	1.3064 (3)	−0.0045 (2)	0.0451 (5)
H12	0.1237	1.3537	−0.0419	0.054*
C18	0.3573 (3)	1.3775 (3)	0.0402 (3)	0.0582 (7)
H13	0.3846	1.4736	0.0337	0.070*
C19	0.4726 (2)	1.3071 (3)	0.0941 (3)	0.0492 (6)
H14	0.5772	1.3555	0.1228	0.059*
Cl1	0.36529 (6)	0.74980 (6)	0.53090 (5)	0.04338 (17)
Cl2	0.22031 (6)	0.73833 (6)	0.12694 (6)	0.04729 (18)
N1	0.92387 (19)	0.6968 (2)	0.40429 (17)	0.0390 (4)
N2	1.14169 (18)	0.9194 (2)	0.39627 (16)	0.0351 (4)
H7	1.170 (3)	0.8472 (19)	0.424 (2)	0.042*
N3	0.70894 (18)	1.13995 (18)	0.19800 (16)	0.0322 (4)
H9	0.746 (3)	1.2193 (17)	0.183 (2)	0.039*
N4	0.53075 (18)	0.96176 (18)	0.19679 (16)	0.0323 (4)
H8	0.4428 (16)	0.905 (2)	0.179 (2)	0.039*
O1	0.85916 (19)	0.38620 (19)	0.15805 (16)	0.0528 (4)
H15	0.9539	0.4251	0.2020	0.079*
H16	0.8531	0.3685	0.0818	0.079*
O2	0.1730 (2)	0.4996 (2)	0.28333 (18)	0.0667 (5)
H17	0.2178	0.5534	0.3568	0.100*
H18	0.1998	0.5510	0.2372	0.100*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0445 (11)	0.0372 (11)	0.0499 (13)	0.0125 (9)	0.0101 (10)	0.0178 (10)
C2	0.0362 (10)	0.0357 (11)	0.0577 (14)	−0.0010 (9)	0.0101 (10)	0.0193 (10)
C3	0.0275 (9)	0.0391 (11)	0.0516 (12)	0.0045 (8)	0.0065 (9)	0.0159 (10)
C4	0.0275 (9)	0.0309 (10)	0.0350 (10)	0.0054 (7)	0.0075 (8)	0.0074 (8)
C5	0.0236 (8)	0.0316 (10)	0.0356 (10)	0.0063 (7)	0.0063 (7)	0.0093 (8)
C6	0.0250 (9)	0.0305 (9)	0.0357 (10)	0.0066 (7)	0.0069 (7)	0.0095 (8)
C7	0.0242 (8)	0.0332 (10)	0.0331 (10)	0.0062 (7)	0.0081 (7)	0.0064 (8)
C8	0.0283 (9)	0.0407 (11)	0.0444 (11)	0.0067 (8)	0.0092 (8)	0.0147 (9)
C9	0.0264 (9)	0.0501 (13)	0.0473 (12)	0.0030 (9)	0.0101 (9)	0.0132 (10)
C10	0.0226 (9)	0.0507 (13)	0.0469 (12)	0.0082 (9)	0.0091 (8)	0.0124 (10)
C11	0.0236 (8)	0.0339 (10)	0.0318 (9)	0.0067 (7)	0.0073 (7)	0.0068 (8)
C12	0.0275 (9)	0.0309 (9)	0.0340 (10)	0.0068 (8)	0.0079 (7)	0.0067 (8)
C13	0.0265 (8)	0.0297 (9)	0.0351 (10)	0.0050 (7)	0.0070 (7)	0.0080 (8)
C14	0.0260 (8)	0.0319 (10)	0.0354 (10)	0.0078 (7)	0.0063 (7)	0.0088 (8)
C15	0.0302 (10)	0.0365 (11)	0.0500 (12)	0.0059 (8)	0.0064 (9)	0.0186 (9)

C16	0.0274 (9)	0.0462 (13)	0.0544 (13)	0.0071 (9)	0.0048 (9)	0.0175 (11)
C17	0.0335 (10)	0.0442 (12)	0.0605 (14)	0.0175 (9)	0.0091 (9)	0.0233 (11)
C18	0.0409 (12)	0.0394 (12)	0.098 (2)	0.0128 (10)	0.0172 (13)	0.0311 (14)
C19	0.0281 (10)	0.0378 (12)	0.0773 (17)	0.0063 (9)	0.0072 (10)	0.0205 (11)
Cl1	0.0327 (3)	0.0454 (3)	0.0491 (3)	0.0099 (2)	0.0054 (2)	0.0164 (2)
Cl2	0.0316 (3)	0.0446 (3)	0.0590 (4)	0.0008 (2)	0.0039 (2)	0.0200 (3)
N1	0.0334 (8)	0.0382 (9)	0.0462 (10)	0.0119 (7)	0.0093 (8)	0.0155 (8)
N2	0.0244 (7)	0.0405 (9)	0.0391 (9)	0.0107 (7)	0.0062 (7)	0.0109 (7)
N3	0.0258 (7)	0.0323 (8)	0.0387 (9)	0.0079 (7)	0.0075 (6)	0.0128 (7)
N4	0.0209 (7)	0.0317 (8)	0.0403 (9)	0.0046 (6)	0.0037 (6)	0.0103 (7)
O1	0.0448 (8)	0.0513 (10)	0.0584 (10)	−0.0012 (7)	0.0115 (7)	0.0217 (8)
O2	0.0752 (12)	0.0547 (11)	0.0581 (11)	−0.0120 (10)	0.0173 (10)	0.0111 (9)

Geometric parameters (Å, °)

C1—N1	1.322 (3)	C12—N1	1.346 (2)
C1—C2	1.391 (3)	C13—N3	1.327 (2)
C1—H1	0.9300	C13—N4	1.346 (2)
C2—C3	1.371 (3)	C13—C14	1.459 (2)
C2—H2	0.9300	C14—C15	1.391 (3)
C3—C4	1.393 (3)	C14—C19	1.393 (3)
C3—H3	0.9300	C15—C16	1.380 (3)
C4—C12	1.412 (3)	C15—H10	0.9300
C4—C5	1.432 (3)	C16—C17	1.369 (3)
C5—C6	1.361 (3)	C16—H11	0.9300
C5—N4	1.379 (2)	C17—C18	1.384 (3)
C6—N3	1.377 (2)	C17—H12	0.9300
C6—C7	1.431 (2)	C18—C19	1.377 (3)
C7—C8	1.391 (3)	C18—H13	0.9300
C7—C11	1.404 (3)	C19—H14	0.9300
C8—C9	1.383 (3)	N2—H7	0.846 (10)
C8—H4	0.9300	N3—H9	0.849 (10)
C9—C10	1.375 (3)	N4—H8	0.848 (10)
C9—H5	0.9300	O1—H15	0.8500
C10—N2	1.321 (3)	O1—H16	0.8500
C10—H6	0.9300	O2—H17	0.8500
C11—N2	1.356 (2)	O2—H18	0.8500
C11—C12	1.452 (3)		
N1—C1—C2	123.78 (18)	C4—C12—C11	119.56 (16)
N1—C1—H1	118.1	N3—C13—N4	108.29 (15)
C2—C1—H1	118.1	N3—C13—C14	126.36 (16)
C3—C2—C1	119.57 (19)	N4—C13—C14	125.35 (16)
C3—C2—H2	120.2	C15—C14—C19	118.88 (17)
C1—C2—H2	120.2	C15—C14—C13	121.12 (17)
C2—C3—C4	118.59 (18)	C19—C14—C13	119.99 (17)
C2—C3—H3	120.7	C16—C15—C14	119.83 (18)
C4—C3—H3	120.7	C16—C15—H10	120.1
C3—C4—C12	117.62 (17)	C14—C15—H10	120.1
C3—C4—C5	126.08 (17)	C17—C16—C15	121.32 (19)

C12—C4—C5	116.25 (18)	C17—C16—H11	119.3
C6—C5—N4	106.64 (16)	C15—C16—H11	119.3
C6—C5—C4	123.25 (17)	C16—C17—C18	119.11 (19)
N4—C5—C4	130.11 (18)	C16—C17—H12	120.4
C5—C6—N3	107.36 (15)	C18—C17—H12	120.4
C5—C6—C7	122.68 (17)	C19—C18—C17	120.6 (2)
N3—C6—C7	129.95 (18)	C19—C18—H13	119.7
C8—C7—C11	119.40 (16)	C17—C18—H13	119.7
C8—C7—C6	125.59 (17)	C18—C19—C14	120.3 (2)
C11—C7—C6	115.00 (17)	C18—C19—H14	119.9
C9—C8—C7	120.23 (19)	C14—C19—H14	119.9
C9—C8—H4	119.9	C1—N1—C12	116.90 (17)
C7—C8—H4	119.9	C10—N2—C11	123.10 (18)
C10—C9—C8	118.2 (2)	C10—N2—H7	116.2 (16)
C10—C9—H5	120.9	C11—N2—H7	120.7 (16)
C8—C9—H5	120.9	C13—N3—C6	108.97 (16)
N2—C10—C9	121.33 (17)	C13—N3—H9	121.2 (16)
N2—C10—H6	119.3	C6—N3—H9	129.8 (16)
C9—C10—H6	119.3	C13—N4—C5	108.73 (16)
N2—C11—C7	117.69 (18)	C13—N4—H8	126.2 (15)
N2—C11—C12	119.08 (17)	C5—N4—H8	124.8 (15)
C7—C11—C12	123.23 (16)	H15—O1—H16	108.0
N1—C12—C4	123.51 (18)	H17—O2—H18	104.1
N1—C12—C11	116.93 (16)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H7···Cl1^{i}	0.846 (10)	2.266 (15)	3.0187 (19)	148 (2)
N3—H9···O1^{ii}	0.849 (10)	1.878 (11)	2.719 (2)	171 (2)
N4—H8···Cl2	0.848 (10)	2.233 (10)	3.078 (2)	175 (2)
O1—H15···O2^{i}	0.85	1.90	2.748 (3)	173
O1—H16···Cl2^{iii}	0.85	2.29	3.110 (2)	163
O2—H17···Cl1	0.85	2.37	3.194 (3)	164
O2—H18···Cl2	0.85	2.38	3.204 (2)	162

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

Fig. 1

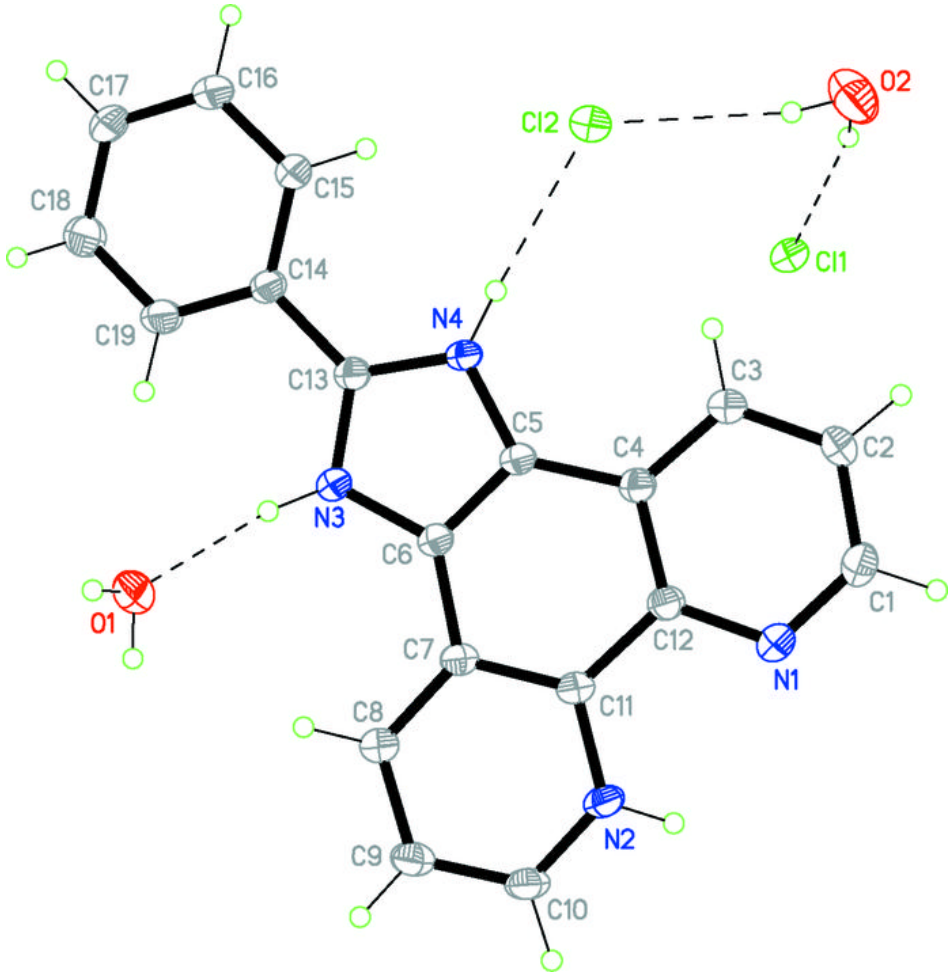
C17
C16
C18
C15
C14
C19
C13
N4
Cl2
O2
Cl1
C3
C5
C4
C2
N3
C6
C1
O1
C12
C7
N1
C11
C8
N2
C9
C10

Fig. 2