

## 2,3-Dithien-2-ylquinoxalin-1-ium perchlorate

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## Key indicators

Single-crystal X-ray study  
T = 100 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$   
R factor = 0.057  
wR factor = 0.150  
Data-to-parameter ratio = 17.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

As a minor by-product from the reaction of copper(II) perchlorate, hydrazine, and 2,3-dithien-2'-ylquinoxaline, the title compound,  $\text{C}_{16}\text{H}_{11}\text{N}_2\text{S}_2^+\cdot\text{ClO}_4^-$ , was synthesized. Its crystal structure has been determined at 100 K. The two independent molecules in the asymmetric unit both display hydrogen bonding from a protonated quinoxaline N atom on the cation to a neighboring O atom on a perchlorate anion.

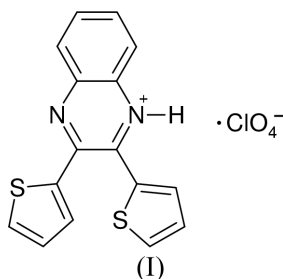
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## Comment

Previous researchers have successfully synthesized 2:1 complexes of 2,3-diphenylquinoxaline and copper(I) by the direct reaction of the quinoxaline, copper(II) perchlorate and hydrazine in ethanol (Datta *et al.*, 2002). Depending on the rate at which the hydrazine was added, the copper in the complex not only bound two 2,3-diphenylquinoxaline moieties (each through a quinoxaline N atom) but also bound either a water molecule or a perchlorate ion (Datta *et al.*, 2002). On the basis of the crystal structure of 2,3-dithien-2'-ylquinoxaline, which has one thienyl ring nearly coplanar with the quinoxaline system (Crundwell, Sayers *et al.*, 2003), we envisioned replacing a water/perchlorate molecule in the  $\text{Cu}^{\text{I}}$  complex with a thienyl ring sulfur from 2,3-dithien-2'-ylquinoxaline, essentially making one of the quinoxaline ligands *N,S*-bidentate. By following the published literature, we were able to synthesize a 2:1 2,3-dithien-2'-ylquinoxaline–copper(I) complex. However, the product did not readily form single crystals suitable for X-ray analysis and did not bind copper through its thienyl ring S atom (evidence seems to indicate that the 2:1 complex has bound perchlorate, as in the analogous complex with 2,3-diphenylquinoxaline). Upon attempted crystallization of the metal–ligand complex from ethanol, a few well defined brown crystals of the title complex, (I), were formed.



There are two molecules of (I) in the asymmetric unit (Fig. 1). Each cation has a quinoxaline N atom that is protonated. The quinoxaline systems both hydrogen bond to a neighboring perchlorate anion (Table 1). The thienyl rings

showed no evidence of flip disorder (Crundwell, Sullivan *et al.*, 2003) and rings in both molecules had different angles with respect to the quinoxaline moiety in the two cations. For the first cation, the dihedral angles between the quinoxaline group and thienyl rings 1 (bearing S1) and 2 (bearing S2) are 33.58 (9) and 57.52 (7)°; for the second cation, the angles are 19.62 (11) and 71.99 (6)° for rings 3 and 4, respectively. Despite the difference in thienyl ring/quinoxaline group dihedral angles, analysis of non-crystallographic symmetry using *PLATON* (Spek, 2003) revealed that the two cations are closely related by a shift and a small rotation, 7.94°.

### Experimental

**Warning:** Metal and organic perchlorates are very dangerous as potential explosives. All reactions should be performed on a millimolar scale with extreme caution. Compound (I) was obtained from the reaction of 1:2 molar amounts of copper(II) perchlorate pentahydrate and 2,3-dithien-2'-ylquinoxaline in refluxing ethanol. In attempts to generate a copper(I)–quinoxaline compound, a slight excess of hydrazine monohydrate in ethanol was pipetted into the refluxing solution (Datta *et al.*, 2002). A fine lemon-yellow precipitate formed [which contained copper, perchlorate and dithienylquinoxaline ligand and is presumably the bis(ligand)copper(I) perchlorate salt]; the solution was then filtered and allowed to evaporate. After four days, more fine yellow powder had formed as well as a minor amount of (I). These brown crystals had well defined morphologies, and were harvested from the vial and washed with ice-cold ethanol to remove the yellow powder. Since only a few crystals of (I) were obtained, a chemical analysis of (I) was not pursued.

#### Crystal data

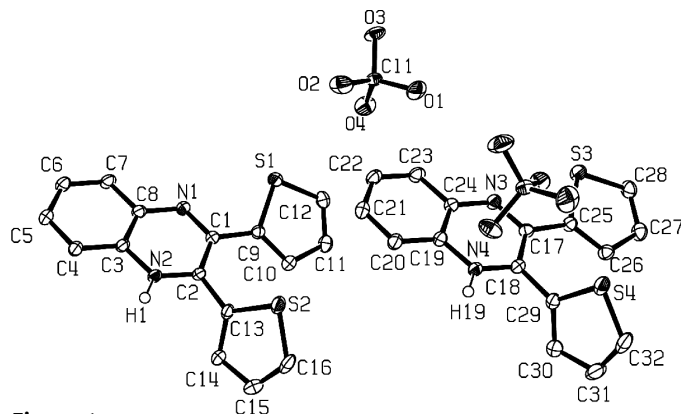
$C_{16}H_{11}N_2S_2^+ \cdot ClO_4^-$	$Z = 4$
$M_r = 394.84$	$D_x = 1.611 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.435 (2) \text{ \AA}$	Cell parameters from 13 920 reflections
$b = 11.199 (2) \text{ \AA}$	$\theta = 2.4\text{--}28.3^\circ$
$c = 15.228 (3) \text{ \AA}$	$\mu = 0.52 \text{ mm}^{-1}$
$\alpha = 86.001 (3)^\circ$	$T = 100 (2) \text{ K}$
$\beta = 73.202 (3)^\circ$	Prism, brown
$\gamma = 72.859 (3)^\circ$	$0.44 \times 0.39 \times 0.14 \text{ mm}$
$V = 1627.7 (5) \text{ \AA}^3$	

#### Data collection

Bruker SMART APEX diffractometer	7974 independent reflections
$\omega$ scans	7341 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan ( <i>SADABS</i> ; Sheldrick, 2003)	$R_{\text{int}} = 0.030$
$T_{\text{min}} = 0.809$ , $T_{\text{max}} = 0.933$	$\theta_{\text{max}} = 28.3^\circ$
16 611 measured reflections	$h = -13 \rightarrow 13$
	$k = -14 \rightarrow 14$
	$l = -20 \rightarrow 20$

#### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + 1.8804P]$
$R[F^2 > 2\sigma(F^2)] = 0.057$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.150$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.18$	$\Delta\rho_{\text{max}} = 0.81 \text{ e \AA}^{-3}$
7973 reflections	$\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$
459 parameters	
H atoms treated by a mixture of independent and constrained refinement	



**Figure 1**

A view of (I) (Farrugia, 1997). Displacement ellipsoids are drawn at the 50% probability level. H atoms not bonded to N atoms have been omitted for clarity, as have the labels for the second perchlorate anion.

**Table 1**

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N2-H1 \cdots O3^i$	0.85 (3)	1.90 (3)	2.728 (3)	166 (3)
$N4-H19 \cdots O7^{ii}$	0.87 (3)	1.85 (3)	2.718 (3)	170 (3)

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

Atoms H1 and H19 were found in difference maps and refined isotropically. The remaining H atoms were included in calculated positions, with a C–H distance of 0.95 Å, and treated as riding, with  $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{carrier atom})$ . The highest peak in the difference map lies close to atom O7 (0.70 Å). The reflection (231) was omitted from the least-squares refinement.

Data collection: *SMART* (Bruker, 1997–1999); cell refinement: (s.u.); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997).

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