

cyclo-Bis[2-methylsulfanyl-6-([1,3,4]thiadiazol-2-ylsulfanylmethyl)pyridinium]diperchlorate

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Key indicators

Single-crystal X-ray study

$T = 301\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

R factor = 0.080

wR factor = 0.051

Data-to-parameter ratio = 13.1

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

In the title compound, $\text{C}_{18}\text{H}_{16}\text{N}_6\text{S}_6^{2+} \cdot 2\text{ClO}_4^-$, the macrocyclic cation shows a twisted conformation and possesses crystallographic twofold symmetry. This conformation is stabilized by intramolecular $\text{N}-\text{H} \cdots \text{N}$ and $\text{C}-\text{H} \cdots \text{N}$ hydrogen bonds. In the crystal, the cations and anions are connected through $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds.

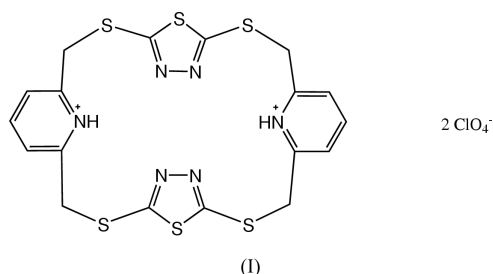
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Comment

Lanthanide(III) complexes, especially those of Gd^{3+} , Eu^{3+} and Tb^{3+} , have a variety of applications as luminescent biomedical diagnostic and therapeutic agents, such as magnetic resonance imaging contrast agents, RNA hydrolysis catalysts and fluorescence imaging agents (Lai *et al.*, 2002; Lam *et al.*, 2001; Li & Wong, 2002). The macrocyclic ligand *cyclo*-bis(2-methylsulfanyl-6-([1,3,4]thiadiazol-2-ylsulfanylmethyl)pyridine) has more than one organic chromophore, which may have effective energy transfer and luminescent enhancement. Moreover, its preorganized structure, with six donor N atoms, may prompt in forming thermodynamically and kinetically stable Ln complexes. These are important features for further molecular exploration and for the development of new pharmaceutical compounds. Herein we report the structure of this macrocyclic ligand in a diprotonated form, as its perchloric salt, (I).



The asymmetric unit of (I) contains one-half of the $\text{C}_{18}\text{H}_{16}\text{N}_6\text{S}_6^{2+}$ cation, with the other half related by a crystallographic twofold axis (S1 and S4 lie on the twofold axis), and a ClO_4^- anion (Fig. 1). The macrocyclic cation exhibits a twisted conformation. This conformation is stabilized by intramolecular $\text{N}-\text{H} \cdots \text{N}$ and $\text{C}-\text{H} \cdots \text{N}$ hydrogen bonds, with $\text{N} \cdots \text{N}$ and $\text{C} \cdots \text{N}$ distances in the ranges 2.999 (4)–3.097 (4) and 2.870 (4)–2.958 (4) Å, respectively (Table 2). The two thiazole rings form dihedral angles of 45.1 (2) and 66.7 (2)° with each pyridine ring. The dihedral angle between the two symmetry-related pyridine rings is 91.1 (2)°, while the two thiazole rings have a dihedral angle of 47.6 (2)°. In the crystal, the cations and anions are linked, through $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds (Table 2), to form a three-dimensional

network structure. The structure is further stabilized by face-to-face π - π -stacking interactions of pyridine rings, with a $Cg \cdots Cg^i$ distance of 3.822 (2) Å [Cg and Cg^i denote the centroids of the pyridine rings at (x, y, z) and $(\frac{1}{2} - x, \frac{1}{2} - y, 1 - z)$, respectively].

Experimental

Compound (I) was prepared according to the procedures reported by Yang & Wong (2001). Crystals suitable for X-ray data collection were obtained by slow evaporation of a $CH_2Cl_2/MeOH$ (3:1; *v:v*) solution of the compound at room temperature.

Crystal data

$C_{18}H_{16}N_6S_6^{2+} \cdot 2ClO_4^-$	$D_x = 1.729 \text{ Mg m}^{-3}$
$M_r = 707.69$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 25 reflections
$a = 12.311(3) \text{ \AA}$	$\theta = 2.5\text{--}14^\circ$
$b = 14.700(2) \text{ \AA}$	$\mu = 0.76 \text{ mm}^{-1}$
$c = 15.205(3) \text{ \AA}$	$T = 301.2 \text{ K}$
$\beta = 98.79(2)^\circ$	Block, yellow
$V = 2719.2(9) \text{ \AA}^3$	$0.45 \times 0.36 \times 0.15 \text{ mm}$
$Z = 4$	

Data collection

Rigaku AFC-7R diffractometer	$R_{\text{int}} = 0.037$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 25^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 14$
$T_{\text{min}} = 0.916, T_{\text{max}} = 0.999$	$k = 0 \rightarrow 17$
2629 measured reflections	$l = -18 \rightarrow 17$
2399 independent reflections	3 standard reflections every 250 reflections
2399 reflections with $I > 0$	intensity decay: 0.1%

Refinement

Refinement on F	$w = 1/[\sigma^2(F_o) + (0.008F_o)^2]$
$R = 0.080$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$wR = 0.051$	$\Delta\rho_{\text{max}} = 0.51 \text{ e \AA}^{-3}$
$S = 1.40$	$\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$
2399 reflections	Extinction correction: Zachariasen type 2 Gaussian isotropic
183 parameters	Extinction coefficient: 5.8529 (2)
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.719 (4)	N2—C7	1.357 (4)
S2—C1	1.743 (4)	N3—N3 ⁱ	1.388 (6)
S2—C8	1.816 (4)	N3—C9	1.292 (4)
S3—C8	1.806 (4)	C2—C3	1.490 (4)
S3—C9	1.742 (4)	C3—C4	1.374 (5)
S4—C9	1.706 (4)	C4—C5	1.377 (5)
N1—N1 ⁱ	1.384 (6)	C5—C6	1.369 (5)
N1—C1	1.295 (4)	C6—C7	1.375 (4)
N2—C3	1.349 (4)	C7—C8	1.484 (5)
C1—S1—C1 ⁱ	86.3 (2)	N2—C3—C4	118.4 (3)
C1—S2—C2	99.6 (2)	C2—C3—C4	122.4 (3)
C8—S3—C9	99.1 (2)	C3—C4—C5	120.0 (3)
C9 ^j —S4—C9	87.1 (2)	C4—C5—C6	119.9 (3)
N1 ⁱ —N1—C1	111.9 (2)	C5—C6—C7	120.3 (3)
C3—N2—C7	123.3 (3)	N2—C7—C6	118.0 (3)
N3 ⁱ —N3—C9	111.9 (2)	N2—C7—C8	119.4 (3)
S1—C1—S2	119.5 (2)	C6—C7—C8	122.5 (3)
S1—C1—N1	115.0 (3)	S3—C8—C7	111.5 (2)
S2—C1—N1	125.5 (3)	S3—C9—S4	120.1 (2)
S2—C2—C3	113.6 (2)	S3—C9—N3	125.3 (3)
N2—C3—C2	119.2 (3)	S4—C9—N3	114.6 (3)

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

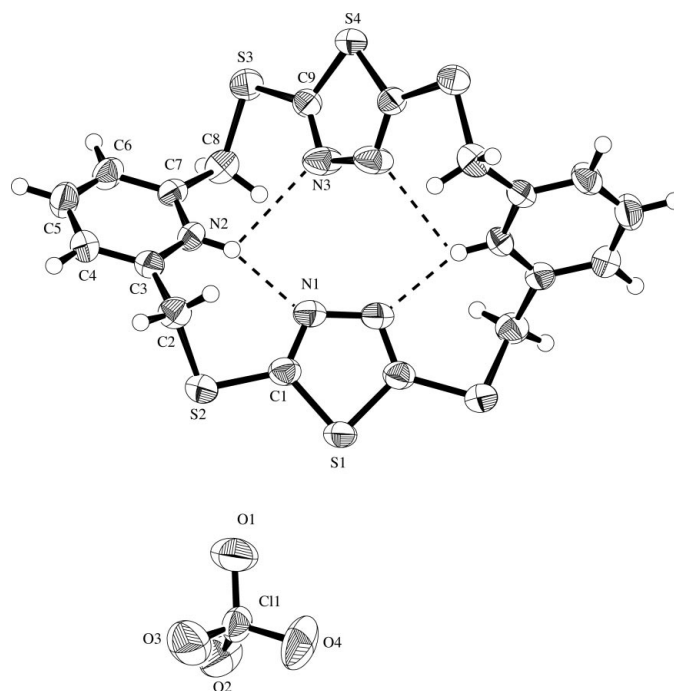


Figure 1
An ORTEP (Johnson, 1976) drawing of (I), showing 50% probability displacement ellipsoids. Only the non-H atoms of the asymmetric unit are labelled.

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2N \cdots N1	0.87	2.20	2.999 (4)	153
N2—H2N \cdots N3	0.87	2.59	3.097 (4)	118
C2—H2B \cdots N1	0.95	2.57	2.958 (4)	105
C8—H8B \cdots N3	0.95	2.47	2.870 (4)	105
C2—H2B \cdots O4 ⁱⁱ	0.95	2.42	3.275 (5)	149
C8—H8A \cdots O1 ⁱⁱⁱ	0.95	2.53	3.463 (5)	165
C8—H8B \cdots O1 ^{iv}	0.95	2.58	3.307 (5)	133
C8—H8B \cdots O3 ^{iv}	0.95	2.50	3.339 (4)	148

Symmetry codes: (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-x, -y, 1 - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} + y, z$.

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with N—H and C—H distances fixed at 0.87 and 0.95 Å, respectively. All unique reflections were included in the refinement on F and, as a result, the R value is high (0.080).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEP* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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