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2,2′:6′,2″-Terpyridinium dinitrate

Claude Berthon and Mikhail S. Grigoriev*‡

CEA Marcoule, DEN/DRCP/SCPS/LCAM, BP 17171, F-30207 Bagnols-sur-Cèze Cedex, France

‡ Permanent address: Institute of Physical Chemistry, Russian Academy of Sciences, 31 Leninsky prospekt, 119991 Moscow, Russia (e-mail: grigoriev@ipc.rssi.ru).

Correspondence e-mail: mg168017@atil.cea.fr

Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.002 Å
R factor = 0.040
wR factor = 0.101
Data-to-parameter ratio = 10.9

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

The doubly protonated terpyridinium cation in the title compound, $C_{15}H_{13}N_3^{2+}\cdot 2NO_3^-$, has a *cis–cis* conformation. Both H atoms attached to the N atoms of the outer rings form hydrogen bonds with the same O atom of one of the two nitrate anions.

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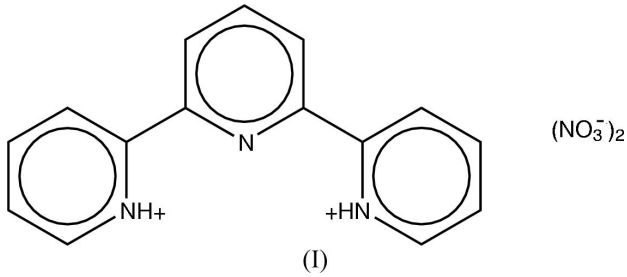
Comment

Terpyridine (terpy) derivatives are one group of promising complexing agents for the reprocessing of spent nuclear fuel. To understand the mechanism of these processes, information is necessary about the structure of all possible species.



(I)

The H_2terpy^{2+} cation in the title compound, (I), has the *cis–cis* conformation. Both H atoms attached to the N atoms of the outer rings form hydrogen bonds with the same O atom of one of the two nitrate anions (Fig. 1, Table 1). In contrast, the non-

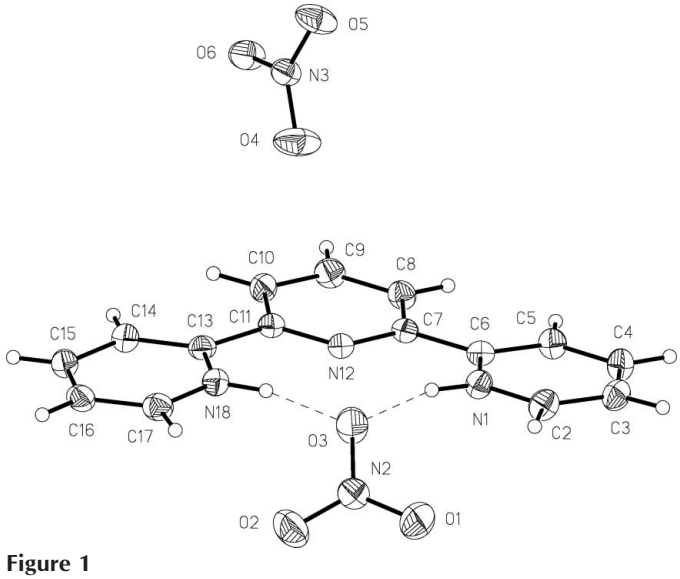


Figure 1
A view of $H_2terpy(NO_3)_2$, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. Dashed lines indicate the hydrogen-bonding interactions.

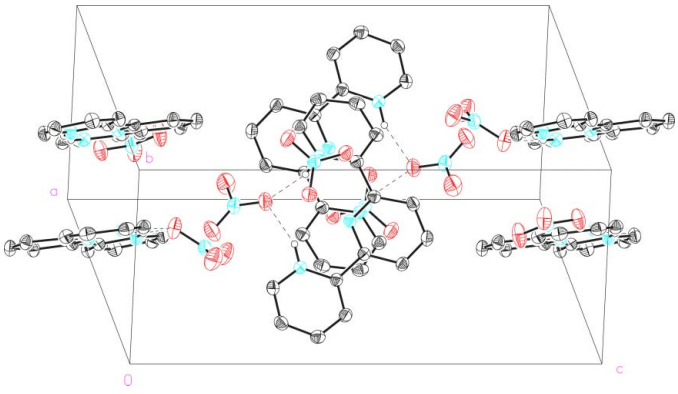


Figure 2
The molecular packing of H_2terpy$(NO_3)_2$. H atoms bonded to C atoms have been omitted for clarity. Dashed lines indicate the hydrogen-bonding interactions.

protonated form of terpyridine has the *trans–trans* conformation (Bessel *et al.*, 1992). $[H_2terpy(NO_3)]^+$ species of similar structure have also been found in several lanthanide complexes (Drew *et al.*, 1998, 2000). ^{1}H NMR spectra prove that the same conformation of the H_2terpy^{2+} cations is conserved in acidic aqueous phases, as well as in pyrrole solutions of $H_2terpy(NO_3)_2$.

Experimental

For the preparation of (I), terpyridine (418 mg) was diluted in methanol (3 ml) and 8.5 *M* HNO_3 (210 µl) was slowly added at room temperature. A white precipitate appeared as soon as the first drop of nitric acid was added. After stirring and centrifugation, the white powder was washed with methanol (2 ml) and placed into a desiccator under vacuum for 48 h. Under these conditions, 560 mg of $H_2terpy(NO_3)_2$ was obtained. Titration of the powder product with 1 *M* NaOH in an ethanol–water (50/50) medium gave a ratio of 1.95 (5) molecules of nitric acid per terpyridine molecule. To obtain single crystals of (I), the powder was recrystallized from pyrrole.

Crystal data

$C_{15}H_{13}N_3^{2+}\cdot 2NO_3^-$
M_r = 359.30
Monoclinic, $P2_1/c$
a = 11.9992 (4) Å
b = 7.8052 (2) Å
c = 16.6679 (3) Å
β = 96.158 (2)°
V = 1552.04 (7) Å^3
Z = 4
D_x = 1.538 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7697 reflections
θ = 1.7–26.4°
μ = 0.12 mm^{-1}
T = 123 (2) K
Fragment, yellow
0.40 × 0.30 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: none
7697 measured reflections
3140 independent reflections
2812 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 26.4°
$h = -14 \rightarrow 14$
$k = -9 \rightarrow 9$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.101
S = 1.03
3140 reflections
288 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.9364P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997*a*)
Extinction coefficient: 0.018 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3	0.90 (2)	1.93 (2)	2.796 (2)	160 (2)
N18—H18···O3	0.92 (2)	1.86 (2)	2.747 (2)	162 (2)

H atoms were located in a difference map and refined without constraints.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL* package (Otwinowski & Minor, 1997); data reduction: *HKL* package; 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: *SHELXTL*.

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