January 2005

2,2':6',2"'-Terpyridine 1,1''-dioxide dihydrate

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2,2′:6′,2″-Terpyridine 1,1″-dioxide dihydrate

The title compound, C_{15}H_{11}N_{3}O_{2}·2H_{2}O, crystallizes with terpyridine dioxide molecules positioned on mirror planes in the space group Pnma. Catemeric assemblages of terpyridine molecules [C—H⋯O—N = 3.386 (4) Å] are linked by bridging water molecules [C—H⋯O = 3.288 (4) and 3.386 (4) Å; O—H⋯O—N = 2.837 (3) and 2.878 (4) Å], giving stacks of two-dimensional undulating motifs.

Comment

Our recent report of the structure of terpyridine trioxide described the contribution of weak C—H⋯acceptor interactions to molecular organization (McKay et al., 2004). Inspection of the structure revealed that each terpyridine trioxide molecule participates in ten C—H⋯O—N contacts with neighboring molecules, creating a three-dimensional network of hydrogen bonds. As a means to further explore the crystal chemistry of the terpyridine chemical framework, we recently prepared and crystallographically determined the structure of terpyridine dioxide dihydrate, (I).

The asymmetric unit of (I) contains one half-molecule of terpyridine dioxide and a water molecule (Fig. 1). Each terpyridine dioxide molecule is positioned on a mirror plane,

Figure 1

The molecular structure and labeling scheme of (I). Unlabeled atoms are related by the symmetry code (x, −y + 1, z). Displacement ellipsoids for the asymmetric unit are shown at the 50% probability level. The symmetry-related water molecule has been omitted.
dimethyldioxirane, was prepared (Murray & Jeyaraman, 1985) by
point for the hydration of terpyridine dioxide. The oxidizing agent,
dioxirane/acetone reaction process and this provides a plausible entry
undertaken to exclude water from the hygroscopic dimethyl-
(I) were obtained by diffusion of diethyl ether solution in dichlor-
forming two O2—H
Each water molecule participates in the crystal packing by
linking adjacent molecular sheets.

The supramolecular motifs observed in the structure of (I)
provide a versatile acceptor that affects the packing prefer-
ences of the components. Inspection of Fig. 2 reveals C3—
H···O1—’N1 contacts that link neighboring terpyridine
molecules. These interactions propagate along the c axis to
form chains consisting of translationally related molecules.
Each water molecule participates in the crystal packing by
forming two O2—H···O1—’N1 contacts that link adjacent
terpyridine N-oxide groups. One such interaction bridges the
one-dimensional terpyridine motifs to give an undulating
molecular sheet (parallel to the bc plane). The second O2—
H···O1—’N1 contact contributes to crystal stabilization by
linking adjacent molecular sheets.

**Experimental**

Compound (I) was prepared using a modification of the procedure
for direct oxidation of pyridine and pyrazine moieties (McKay et al.,
2001). Dimethyldioxirane (17.71 ml, 0.08 M) in acetone was stirred
with terpyridine (150.4 mg, 0.6447 mol, Aldrich 98%) in acetone
(2 ml, Fisher reagent grade) for 5 d at 300 K. Filtration of the mixture
provided terpyridine dioxide as a colorless solid [92.2%, 157.6 mg;
505–506 K (Thummel & Jahng, 1985)]. Crystals of (I) were obtained by
diffusion of diethyl ether solution in dichloro-
omethane at room temperature. Exhaustive measures were not
undertaken to exclude water from the hygroscopic dimethyl-
dioxirane/acetone reaction process and this provides a plausible entry
point for the hydration of terpyridine dioxide. The oxidizing agent,
dimethyldioxirane, was prepared (Murray & Jeyaraman, 1985) by
reacting potassium peroxomonosulfate (0.0390 mol) and NaHCO3
(0.138 mol) in acetone (38.4 ml) and water (50 ml). Vigorous stirring
of the mixture at 263 K followed by distillation (40–100 Torr) at
ambient temperature resulted in 0.06–0.08 M dimethyldioxirane, as
verified by titration against thioanisole.

**Figure 2**

View of the molecular packing of (I), projected down the a axis, showing
the hydrogen-bond network. Hydrogen bonds are shown as dotted lines.

The OH and aryl H atoms were located in a difference density map
and refined isotropically. The H-atom positions and Uiso values were
refined and no constraints to the H atoms were applied during the
refinement process [C—H = 0.87 (3)–0.91 (3) Å]. After refinement,
the C—H bonds were adjusted to 1.08 Å for subsequent hydrogen-
bond analysis (Fig. 2).

**Table 1**

<table>
<thead>
<tr>
<th>Bond</th>
<th>d (Å)</th>
<th>d (Å)</th>
<th>d (Å)</th>
<th>d (Å)</th>
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<td>1.476 (3)</td>
<td>C6—N2</td>
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<tr>
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<td>C4—C5</td>
<td>1.476 (3)</td>
<td>C6—C7</td>
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<tr>
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**Table 2**

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The symmetry codes are: (i) x, y, z; (ii) 2−x, 1−y, 1−z; (iii) x, y, 1+z.
Data collection: XSCANS (Bruker, 1999); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: X-SEED (Barbour, 2001); software used to prepare material for publication: X-SEED.

Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund Type B and the National Science Foundation (DMR-9414042) for support of this crystallographic investigation.

References