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# Tris(dimethylammonium) tris(pyridine-2,6-dicarboxylato-$\kappa^3N,O,O'$)europate(III) dihydrate

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**Key indicators**

Single-crystal X-ray study
$T$ = 292 K
Mean $\sigma$(C–C) = 0.004 Å
Disorder in solvent or counterion
$R$ factor = 0.031
$wR$ factor = 0.073
Data-to-parameter ratio = 14.9

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



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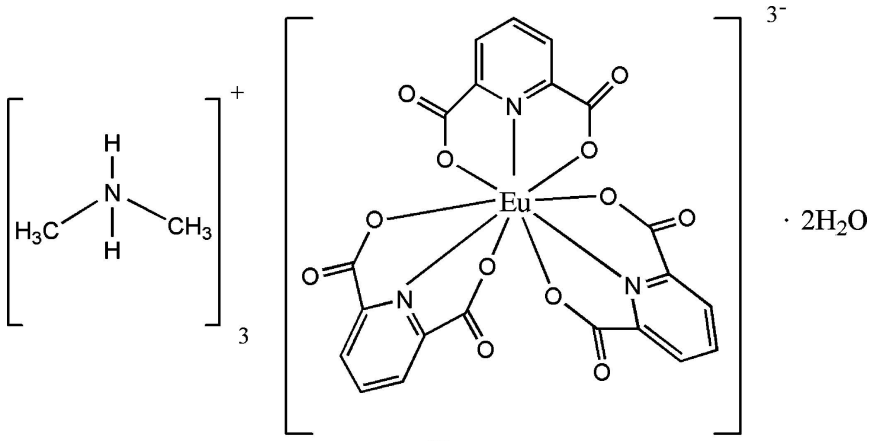
In the title compound, $(C_2H_8N)_3[Eu(C_7H_3NO_4)_3]\cdot 2H_2O$, the complex anion lies on a crystallographic twofold rotation axis and the $Eu^{III}$ atom is coordinated by three N and six O atoms from three pyridine-2,6-dicarboxylate ligands, forming a distorted tricapped trigonal prismatic geometry. Dimethylammonium cations and non-coordinated water molecules show positional disorder. The crystal structure is stabilized by intermolecular N—H···O and O—H···O hydrogen bonds.

## Comment

The crystal structure of complexes containing the pyridine-2,6-dicarboxylate (DPC) $Eu^{III}$ anion, *viz.* $Na_3[Eu(DPC)_3]\cdot 14H_2O$ (Li *et al.*, 1993) and $Cs_3[Eu(DPC)_3]\cdot 9H_2O$ (Brayshaw *et al.*, 1995), have been reported previously and its fluorescence has been studied (Yi *et al.*, 2002). We report here the structure of the title compound, (I), which was obtained unexpectedly by hydrothermal synthesis.




(I)

The molecular structure of (I) is shown in Fig. 1. There is a crystallographic twofold rotation axis passing through atoms Eu, N2 and C10. The $Eu^{III}$ atom exists in a distorted tricapped trigonal prismatic coordination environment, defined by three N and six O atoms from three pyridine-2,6-dicarboxylate ligands. The Eu—N and Eu—O bond lengths (Table 1) are in good agreement with those reported for similar complexes (Li *et al.*, 1993; Brayshaw *et al.*, 1995). There are one and a half dimethylammonium cations in the asymmetric unit. The N5/C14/C15 cation is is disordered over an inversion center, and the position is shared by two water molecules (O9 and O10), each with half-occupancy. Cations and anions are connected through N—H···O hydrogen bonds (Table 2). There are also O—H···O hydrogen bonds involving the non-coordinated

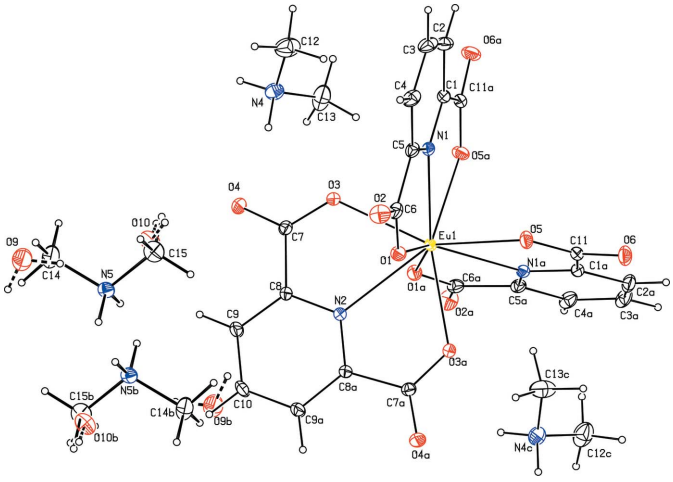



**Figure 1**
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level. Water molecules and one of the cations are disordered and occupy the same position with an occupancy of 0.5. [Symmetry codes: (*a*) $1-x, y, \frac{3}{2}-z$; (*b*) $1-x, -y, 1-z$; (*c*) $1-x, y, \frac{3}{2}-z$].

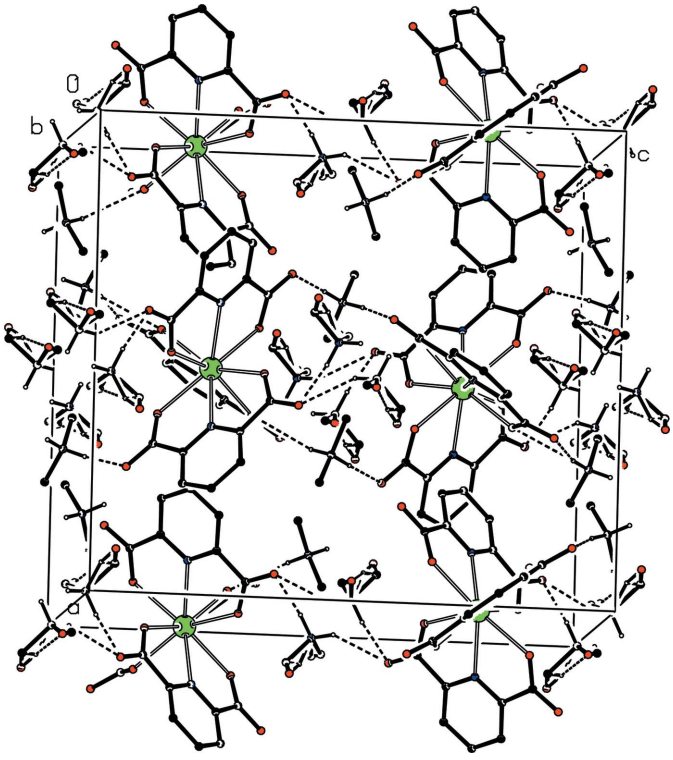



**Figure 2**
A view of the hydrogen bonding (dashed lines) in (I). H atoms have been omitted unless they are involved in hydrogen bonds.

water molecules. Intermolecular hydrogen bonds give rise to a two-dimensional network (Fig. 2).

## Experimental

The title compound, (I), was obtained unexpectedly. A mixture of $Eu(NO_3)_3$, H*L* [H*L* is bis(salicylaldehyde) 2,6-dipicolinoylhydrazone], $H_2O$ and dimethylformamide (DMF) in a 1:2.5:50:50 molar ratio was stirred for 2 h at 353 K, sealed in a 15 ml Teflon-lined stainless steel bomb, kept at 453 K for 96 h, and then cooled slowly to ambient temperature. Colorless block-shaped crystals formed by slow evaporation of the solvent at room temperature over approximately two weeks. X-ray crystal analysis of (I) revealed the unexpected structure, suggesting that pyridine-2,6-dicarboxylic acid and dimethylamine were produced by decomposition of H*L* and DMF, respectively.

### *Crystal data*

$(C_2H_8N)[Eu(C_7H_3NO_4)_3]\cdot 2H_2O$
$M_r = 821.59$
Orthorhombic, *Pbcn*
$a = 16.9780\ (13)$ Å
$b = 10.7099\ (8)$ Å
$c = 18.6170\ (14)$ Å
$V = 3385.2\ (4)$ Å$^3$
$Z = 4$
$D_x = 1.612$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 1.93$ mm$^{-1}$
$T = 292\ (2)$ K
Block, colorless
0.30 × 0.20 × 0.20 mm

### *Data collection*

Bruker SMART CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SHELXTL*; Bruker, 2001)
$T_{min} = 0.596$, $T_{max} = 0.699$
19609 measured reflections
3695 independent reflections
2746 reflections with $I > 2\sigma(I)$
$R_{int} = 0.070$
$\theta_{max} = 27.0°$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.073$
$S = 0.99$
3695 reflections
248 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.40$ e Å$^{-3}$
$\Delta\rho_{min} = -1.18$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Eu1—O5 | 2.442 (2) | Eu1—N1 | 2.535 (2) |
| Eu1—O3 | 2.4456 (18) | Eu1—N2 | 2.540 (3) |
| Eu1—O1 | 2.4667 (19) | | |
| O5—Eu1—O5$^{i}$ | 87.08 (11) | O5—Eu1—O1$^{i}$ | 126.71 (6) |
| O5—Eu1—O3 | 148.78 (6) | O3—Eu1—O1$^{i}$ | 77.35 (7) |
| O5$^{i}$—Eu1—O3 | 78.27 (7) | O5—Eu1—O1 | 78.36 (7) |
| O3—Eu1—O3$^{i}$ | 126.56 (8) | O3—Eu1—O1 | 88.48 (7) |

Symmetry code: (i) $-x+1, y, -z+\frac{3}{2}$.

**Table 2**
Hydrogen-bond geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N4—H4*A*···O3 | 0.90 | 2.43 | 3.118 (3) | 134 |
| N4—H4*A*···O4 | 0.90 | 1.91 | 2.785 (3) | 163 |
| N4—H4*B*···O2$^{ii}$ | 0.90 | 1.82 | 2.710 (4) | 170 |
| N5—H5*A*···O6$^{ii}$ | 0.90 | 1.73 | 2.625 (5) | 172 |
| N5—H5*B*···O6$^{iii}$ | 0.90 | 2.20 | 2.949 (5) | 140 |
| O9—H9*B*···O10 | 0.86 | 2.08 | 2.90 (1) | 161 |
| O10—H10*A*···O5$^{ii}$ | 0.83 | 2.22 | 2.97 (2) | 151 |
| O10—H10*B*···O4 | 0.82 | 2.39 | 3.15 (1) | 153 |

Symmetry codes: (ii) $x, -y+1, z-\frac{1}{2}$; (iii) $-x+1, y-1, -z+\frac{3}{2}$.

Two water molecules (O9 and O10) and two methyl groups of one of the cations (N5/C14/C15) occupy nearly the same positions, and are disordered with an occupancy of 0.5, close to an inversion center. H atoms attached to C and N atoms were refined using a riding

model, with C—H = 0.93–0.96 Å, N—H = 0.90 Å and $U_{iso}$(H) = 1.2$U_{eq}$(C,N) or 1.5$U_{eq}$(methyl C). The H atoms of water molecules were located in difference maps, and refined with the constraints O—H = 0.82–0.86 Å, H···H = 1.35 Å and $U_{iso}$(H) = 1.5$U_{eq}$(O). The deepest hole is located near atom Eu1.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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