

Dihydronium 2,6-diaminopyridinium tris(2,6-pyridinedicarboxylato)ytterbate(III) dihydrate

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Key indicators

Single-crystal X-ray study

$T = 115\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.028

w R factor = 0.059

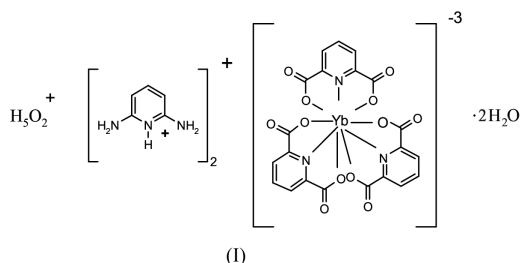
Data-to-parameter ratio = 19.3

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

The reaction of ytterbium(III) chloride with a self-assembling pyridine-containing ligand system, $[\text{H}_2\text{pyda}]^{2+}[\text{pydc}]^{2-}$ [pyda is 2,6-diaminopyridine ($\text{C}_5\text{H}_7\text{N}_3$) and pydcH_2 is 2,6-pyridinedicarboxylic acid ($\text{C}_7\text{H}_5\text{NO}_4$)], in water leads to the formation of the title Yb^{III} complex, $(\text{H}_5\text{O}_2)(\text{Hpyda})_2[\text{Yb}(\text{pydc})_3]\cdot 2\text{H}_2\text{O}$. The Yb atom lies on a twofold rotation axis and is nine-coordinate with a distorted tricapped trigonal-prismatic geometry. The formula unit of the complex contains one $(\text{H}_5\text{O}_2)^+$ dihydranium cation on a twofold rotation axis, two protonated pyda molecules and two water molecules.

Comment

Recently, we have reported the synthesis of a novel self-assembling pyridine-containing ligand system (Moghimi, Ranjbar, Aghabozorg, Jalali, Shamispur, Yap & Rahbarnoochi, 2002). We have succeeded in making mononuclear, binuclear and polymeric complexes of this ligand. Some of these complexes possess an $[\text{Hpyda}]^+$ unit as a counter-ion (pyda is 2,6-diaminopyridine); this is the case for $[\text{Hpyda}][\text{Cr}(\text{pydc})_2]\cdot\text{H}_2\text{pydc}\cdot 0.5\text{H}_2\text{O}$ (Ranjbar *et al.*, 2001*a*), $[\text{Hpyda}]_2[\text{Cu}(\text{pydc})_2]\cdot\text{H}_2\text{O}$ (Ranjbar, Taghavipur *et al.*, 2002) and $[\text{Hpyda}][\text{Zn}(\text{Hpydc})(\text{pydc})_3]\cdot 3\text{H}_2\text{O}$ (Ranjbar, Aghabozorg *et al.*, 2002) (pydcH_2 is 2,6-pyridinedicarboxylic acid). However, $[\text{Bi}_2(\text{pydc})_2\text{Cl}(\text{H}_2\text{O})]_n$ (Ranjbar *et al.*, 2001*b*) is a polymeric complex without an $[\text{Hpyda}]^+$ counter-ion. Our goal was the generation of a self-assembling coordination compound. The presence of $[\text{H}_2\text{pyda}]^{2+}$ as counter-ion in the starting material causes the $[\text{pydc}]^{2-}$ ligand to form different complexes from those that have been reported before, such as $\text{Ln}_2(\text{pydc})_3(\text{H}_2\text{O})_3$ (Brouca-Cabarrecq *et al.*, 2002) and $[\text{Hpyda}]_2[\text{La}_2(\text{pydc})_4(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ (Moghimi, Ranjbar, Aghabozorg, Jalali, Shamispur & Chadha *et al.*, 2002).



The anion of the title complex, (I), is nine-coordinate with a distorted tricapped trigonal-prismatic geometry. The Yb atom lies on a twofold rotation axis. The average Yb—O and Yb—N bond lengths are 2.369 (18) and 2.453 (2) Å, respectively, in agreement with previous reports (Fernandes *et al.*, 2001). The dihedral angle between the plane of the twofold symmetric ligand and each of the others is 75.24 (3)°.

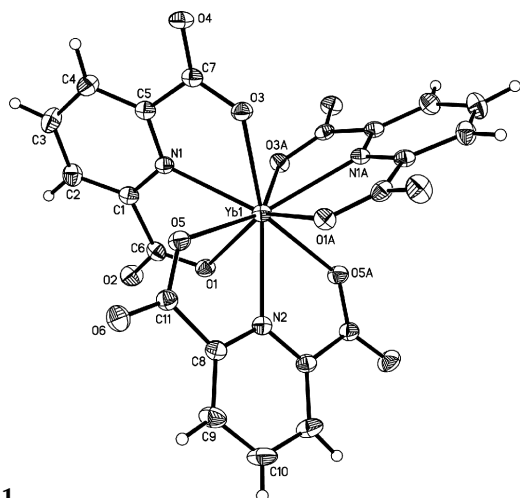


Figure 1
The structure of the anion of the title complex, with displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (A) $\frac{1}{2} - x, y, \frac{1}{2} - z$.]

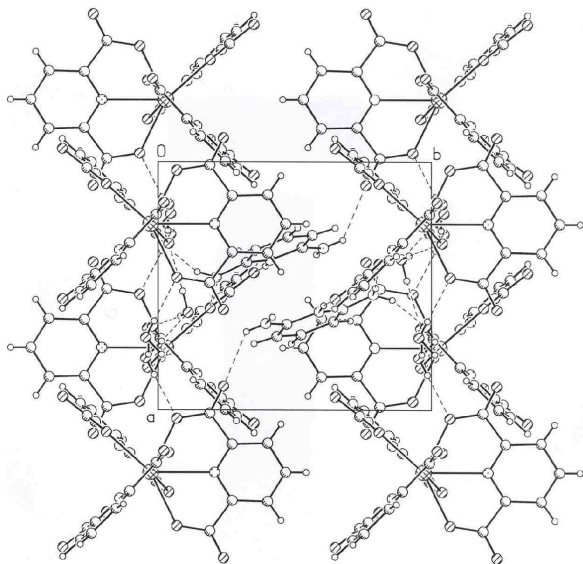


Figure 2
A packing diagram of the title complex. Hydrogen bonds are shown as dashed lines.

Of particular interest is the presence of the dihydronium cation, $(\text{H}_5\text{O}_2)^+$, in the structure. This lies on a twofold rotation axis. The $(\text{H}_5\text{O}_2)^+$ ion is known in $\text{HBr}\cdot 2\text{H}_2\text{O}$ (Kearly, 1986), where the H-atom bridge is nearly symmetrical, but in other cases the O—H—O distances differ considerably. Modeling of the $(\text{H}_5\text{O}_2)^+$ ion from *ab initio* MP2 computations (Ojamae *et al.*, 1995) has shown that the two O—H bridging bond lengths are 1.20 Å and the O—H—O bridging bond angle is 173.5°. The O—H—O bridge in the title complex is almost linear (170°) and the O1W—H1WC bond length is 1.22 Å, representing a very strong and symmetrical hydrogen-bonding interaction between formal H_2O and H_3O^+ units.

Experimental

To a solution of $[\text{H}_2\text{pyda}][\text{pydc}]$ (0.5 g, 1.8 mmol) in water (100 ml) was added a solution of $\text{YbCl}_3\cdot 6\text{H}_2\text{O}$ (0.234 g, 0.6 mmol) in water

(20 ml) and the resulting yellow solution was stirred for 1 min. The pale-yellow solution was left to evaporate slowly at room temperature. After 2 d, yellow prismatic crystals were isolated; yield 68.3%, m.p. 531–533 K.

Crystal data

$(\text{H}_5\text{O}_2)(\text{C}_5\text{H}_8\text{N}_3)_2\text{Yb}(\text{C}_7\text{H}_3\text{NO}_4)_3\cdot 2\text{H}_2\text{O}$
 $M_r = 961.71$
 Monoclinic, $P2_1/n$
 $a = 9.6357$ (5) Å
 $b = 10.5295$ (5) Å
 $c = 17.7932$ (9) Å
 $\beta = 94.953$ (1)°
 $V = 1798.54$ (16) Å³
 $Z = 2$

$D_x = 1.776$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 9085 reflections
 $\theta = 2.3$ – 30.0°
 $\mu = 2.69$ mm⁻¹
 $T = 115$ (2) K
 Prism, yellow
 0.25 × 0.20 × 0.15 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1998)
 $T_{\min} = 0.552$, $T_{\max} = 0.695$
 16540 measured reflections

5008 independent reflections
 4154 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\max} = 30.0^\circ$
 $h = -13 \rightarrow 13$
 $k = -11 \rightarrow 14$
 $l = -24 \rightarrow 24$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.059$
 $S = 0.89$
 5008 reflections
 259 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0305P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 3.83$ e Å⁻³
 $\Delta\rho_{\min} = -0.73$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------------------|-------------|-------------------------|-------------|
| Yb1—O1 | 2.3513 (17) | Yb1—N1 | 2.447 (2) |
| Yb1—O5 | 2.3768 (18) | Yb1—N2 | 2.465 (3) |
| Yb1—O3 | 2.3799 (19) | | |
| O1—Yb1—O1 ⁱ | 145.14 (10) | O5—Yb1—N1 ⁱ | 138.90 (7) |
| O1—Yb1—O5 | 86.36 (6) | O3—Yb1—N1 ⁱ | 73.88 (7) |
| O1—Yb1—O5 ⁱ | 79.04 (6) | O1—Yb1—N1 | 65.66 (7) |
| O5—Yb1—O5 ⁱ | 129.90 (10) | O5—Yb1—N1 | 70.03 (7) |
| O1—Yb1—O3 ⁱ | 77.00 (7) | O3—Yb1—N1 | 65.21 (7) |
| O5—Yb1—O3 ⁱ | 143.85 (6) | N1 ⁱ —Yb1—N1 | 121.77 (10) |
| O1—Yb1—O3 | 130.85 (6) | O1—Yb1—N2 | 72.57 (5) |
| O5—Yb1—O3 | 78.41 (7) | O5—Yb1—N2 | 64.95 (5) |
| O3 ⁱ —Yb1—O3 | 88.51 (9) | O3—Yb1—N2 | 135.75 (5) |
| O1—Yb1—N1 ⁱ | 134.72 (6) | N1—Yb1—N2 | 119.12 (5) |

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

The largest residual density peak lies near the Yb atom and is due to considerable absorption effects which could not be completely corrected. H atoms bonded to O atoms were located in a difference Fourier map, and others were positioned geometrically (C—H = 0.95 Å). All were included in the refinement in a riding-model approximation, with $U_{\text{iso}}(\text{H})$ values set at 1.2 U_{eq} of the parent atom. O—H distances are in the range 0.72–1.22 Å, except for the bridging H atom, for which O—H = 1.22 Å; N—H distances are in the range 0.72–0.94 Å.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT-Plus (Bruker, 1998); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Sheldrick, 1998); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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