

Hossein Aghabozorg,\* Bahar Nakhjavan, Mohammad Ghadermazi and Farshid Ramezanipour

Department of Chemistry, Teacher Training University, 49 Mofateh Avenue, 15614 Tehran, Iran

Correspondence e-mail: aghabozorg@saba.tmu.ac.ir

#### Key indicators

Single-crystal X-ray study  
 $T = 120$  K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.012$  Å  
 H-atom completeness 99%  
 Disorder in solvent or counterion  
 $R$  factor = 0.053  
 $wR$  factor = 0.130  
 Data-to-parameter ratio = 16.6

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

## Bis(propane-1,3-diaminium) tris(pyridine-2,6-dicarboxylato- $\kappa^3\text{O},\text{N},\text{O}'$ )cerate(III) nitrate 3.5-hydrate

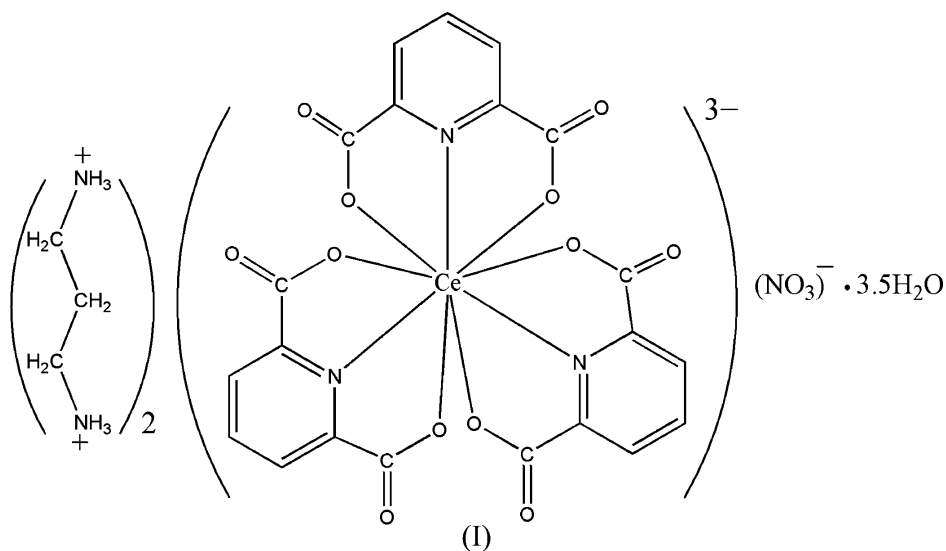
The title compound,  $(\text{C}_3\text{H}_{12}\text{N}_2)_2[\text{Ce}(\text{C}_7\text{H}_3\text{NO}_4)_3](\text{NO}_3) \cdot 3.5\text{H}_2\text{O}$ , is a nine-coordinate Ce complex obtained from a proton-transfer compound. The molecular structure contains three pyridine-2,6-dicarboxylate species as tridentate ligands and two propane-1,3-diaminium cations as counter-ions. The asymmetric unit also contains one nitrate anion and 3.5 uncoordinated water molecules. In the crystal structure, a wide range of hydrogen-bonding interactions connect the various fragments into a supramolecular structure.

Received 11 May 2006

Accepted 6 June 2006

#### Comment

In recent years, several lanthanide complexes containing anionic forms of pyridine-2,6-dicarboxylic acid ( $\text{pydcH}_2$ ) have been synthesized (Lü *et al.*, 2005; Ghosh & Bharadwaj, 2005, 2004; Brouca-Cabarrecq *et al.*, 2002). We have been involved in the study of the coordination chemistry of a large number of elements, including lanthanides, using our proton-transfer compounds. The most recent proton-transfer compound we have synthesized is  $(\text{PDAH}_2)(\text{pydc})\text{pydcH}_2 \cdot 2.5\text{H}_2\text{O}$  ( $\text{PDAH}_2$  is propane-1,3-diamine,  $\text{pydc}$  is pyridine-2,6-dicarboxylate and  $\text{pydcH}_2$  is pyridine-2,6-dicarboxylic acid) (Aghabozorg *et al.*, 2006), which was used for the preparation of the metal-organic complex of the title compound, (I).



The structure of (I) shows only the anionic fragment of the starting proton-transfer compound, which is linked to the Ce atom as a ligand; the cationic species is an uncoordinated fragment (Fig. 1). The  $\text{Ce}^{\text{III}}$  atom is coordinated by three tridentate  $(\text{pydc})^{2-}$  ligands. Two  $(\text{PDAH}_2)^{2+}$  cations, one

nitrate anion and 3.5 water molecules are also observed in the crystal structure as uncoordinated fragments. It should be noted that the starting proton-transfer compound contains both neutral and dianionic forms of pydcH<sub>2</sub>, while complex (I) includes only the dianionic form of this diacid.

The atoms of the nitrate ion are disordered over two positions. Atoms C26 and C27 of one of the (PDAH<sub>2</sub>)<sup>2+</sup> fragments also occupy two positions, showing further disorder in the structure. The central Ce<sup>III</sup> atom is linked to the ligands by Ce—O and Ce—N bonds, for which the distances are almost in the same range as the Ce complexes (Moghimi *et al.*, 2002; Sheshmani *et al.*, 2005) of our other proton-transfer compound, (pydaH)(pydcH) (pyda is 2,6-pyridinediamine) (Aghabozorg *et al.*, 2005). All Ce—O bonds are nearly equal to each other, and the Ce—N bonds are almost the same (Table 1).

A noticeable characteristic of the structure of (I) is a large number of hydrogen-bonding interactions throughout the crystal structure. N—H···O and O—H···O hydrogen bonds connect the components of the crystal structure. The D···A distances of the N—H···O hydrogen bonds are in the range 2.68 (1)–3.22 (1) Å, showing both strong and weak interactions. The O—H···O hydrogen bonds have D···A distances in the range 2.72 (1)–2.946 (9) Å. These interactions result in the formation of a supramolecular structure based on a hydrogen-bonded network.

Experimental

A solution of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O in water (20 ml) was added to an aqueous solution (20 ml) of (PDAH<sub>2</sub>)(pydc).pydcH<sub>2</sub>·2.5H<sub>2</sub>O in a 1:2 molar ratio. Crystals of (I) were obtained after allowing the mixture to stand for one week at room temperature.

Crystal data

(C<sub>3</sub>H<sub>12</sub>N<sub>2</sub>)<sub>2</sub>[Ce(C<sub>7</sub>H<sub>3</sub>NO<sub>4</sub>)<sub>3</sub>]  
(NO<sub>3</sub>)<sub>3</sub>·3.5H<sub>2</sub>O  
M<sub>r</sub> = 912.29  
Triclinic, P1̄  
a = 10.4071 (10) Å  
b = 13.7063 (14) Å  
c = 14.3438 (14) Å  
α = 65.385 (5)°  
β = 80.327 (5)°  
γ = 78.883 (5)°  
V = 1816.4 (3) Å<sup>3</sup>  
Z = 2  
D<sub>x</sub> = 1.669 Mg m<sup>-3</sup>  
Mo Kα radiation  
μ = 1.34 mm<sup>-1</sup>  
T = 120 (2) K  
Prism, colourless  
0.40 × 0.20 × 0.20 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer  
φ and ω scans  
Absorption correction: multi-scan (SADABS; Sheldrick, 1998)  
T<sub>min</sub> = 0.732, T<sub>max</sub> = 0.769  
16675 measured reflections  
8575 independent reflections  
6719 reflections with I > 2σ(I)  
R<sub>int</sub> = 0.036  
θ<sub>max</sub> = 28.0°

Refinement

Refinement on F<sup>2</sup>  
R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.053  
wR(F<sup>2</sup>) = 0.130  
S = 1.06  
8575 reflections  
518 parameters  
H-atom parameters constrained  
w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.04P)<sup>2</sup> + 7.9P]  
where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3  
(Δ/σ)<sub>max</sub> < 0.001  
Δρ<sub>max</sub> = 3.01 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -1.45 e Å<sup>-3</sup>

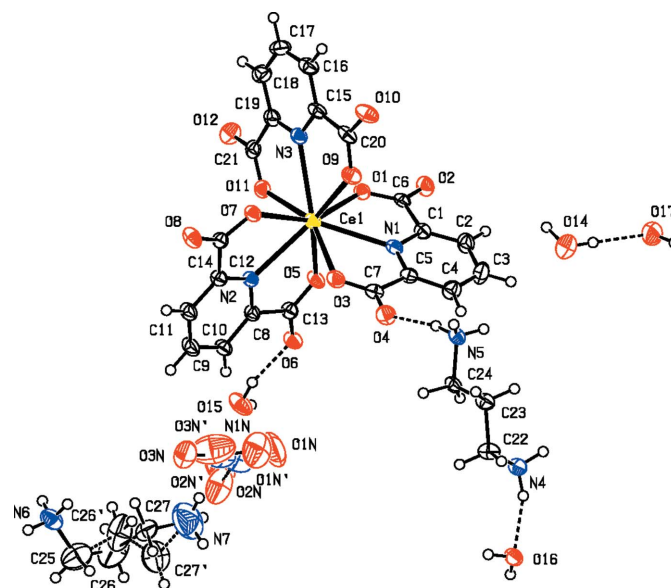


Figure 1 The asymmetric unit of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines. Both disorder components of the nitrate anion and one of the propane-1,3-diaminium cations are shown.

Table 1 Selected geometric parameters (Å, °).

Ce1—O5	2.504 (5)	Ce1—O9	2.534 (5)
Ce1—O11	2.505 (5)	Ce1—N2	2.606 (6)
Ce1—O7	2.509 (5)	Ce1—N1	2.629 (6)
Ce1—O1	2.510 (5)	Ce1—N3	2.635 (6)
Ce1—O3	2.523 (5)		
O5—Ce1—O11	79.91 (17)	O1—Ce1—N2	131.76 (17)
O5—Ce1—O7	124.48 (16)	O3—Ce1—N2	74.87 (17)
O11—Ce1—O7	88.83 (16)	O9—Ce1—N2	137.24 (17)
O5—Ce1—O1	74.42 (16)	O5—Ce1—N1	74.54 (17)
O11—Ce1—O1	74.98 (16)	O11—Ce1—N1	134.06 (17)
O7—Ce1—O1	153.04 (16)	O7—Ce1—N1	137.07 (17)
O5—Ce1—O3	86.35 (17)	O1—Ce1—N1	61.77 (17)
O11—Ce1—O3	153.34 (17)	O3—Ce1—N1	61.57 (17)
O7—Ce1—O3	80.25 (17)	O9—Ce1—N1	74.30 (18)
O1—Ce1—O3	123.10 (17)	N2—Ce1—N1	119.10 (18)
O5—Ce1—O9	148.84 (18)	O5—Ce1—N3	136.61 (17)
O11—Ce1—O9	123.32 (17)	O11—Ce1—N3	62.10 (18)
O7—Ce1—O9	80.02 (17)	O7—Ce1—N3	77.34 (17)
O1—Ce1—O9	90.90 (17)	O1—Ce1—N3	76.05 (16)
O3—Ce1—O9	78.85 (17)	O3—Ce1—N3	136.78 (18)
O5—Ce1—N2	61.67 (16)	O9—Ce1—N3	61.23 (18)
O11—Ce1—N2	78.50 (17)	N2—Ce1—N3	123.91 (18)
O7—Ce1—N2	62.82 (16)	N1—Ce1—N3	116.98 (18)

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4B···O16	0.91	1.95	2.819 (8)	159
N4—H4C···O15 <sup>i</sup>	0.91	2.02	2.924 (10)	173
N4—H4D···O1 <sup>ii</sup>	0.91	2.01	2.892 (9)	163
N5—H5A···O4	0.91	1.90	2.800 (10)	168
N5—H5B···O6 <sup>ii</sup>	0.91	1.98	2.863 (8)	164
N5—H5C···O7 <sup>iii</sup>	0.91	1.95	2.858 (9)	173
N5—H5C···O8 <sup>iii</sup>	0.91	2.54	3.048 (8)	116

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N6–H6A···O10 <sup>iv</sup>	0.91	1.85	2.750 (10)	175
N6–H6B···O14 <sup>v</sup>	0.90	2.05	2.86 (1)	149
N6–H6C···O3 <sup>vi</sup>	0.90	2.51	3.179 (9)	131
N6–H6C···O4 <sup>vi</sup>	0.90	1.95	2.842 (10)	171
N7–H7A···O2N <sup>vii</sup>	0.94	2.11	2.95 (1)	148
N7–H7B···O15 <sup>vii</sup>	0.90	2.34	3.22 (1)	169
N7–H7C···O12 <sup>viii</sup>	0.90	2.02	2.68 (1)	130
O14–H14A···O16 <sup>ix</sup>	1.00	1.88	2.875 (10)	174
O14–H14B···O17	0.90	2.00	2.90 (10)	179
O15–H15A···O8 <sup>x</sup>	0.91	2.23	2.946 (9)	135
O15–H15B···O6	0.92	1.93	2.816 (9)	161
O16–H16A···O10 <sup>xi</sup>	0.91	1.88	2.732 (7)	154
O16–H16B···O2 <sup>xiii</sup>	0.85	1.88	2.732 (7)	176
O17–H17B···O12 <sup>xii</sup>	1.09	2.00	2.72 (1)	120

Symmetry codes: (i)  $x, y-1, z$ ; (ii)  $-x+1, -y+1, -z+1$ ; (iii)  $-x, -y+1, -z+1$ ; (iv)  $x, y+1, z-1$ ; (v)  $x-1, y+1, z-1$ ; (vi)  $-x, -y+2, -z$ ; (vii)  $-x+1, -y+2, -z$ ; (viii)  $x, y, z-1$ ; (ix)  $x, y, z+1$ ; (x)  $x+1, y, z$ ; (xi)  $x+1, y, z-1$ ; (xii)  $x+1, y-1, z$ .

The highest final difference electron-density peak and the deepest hole are located 0.94 and 0.58 Å from Ce1 and N7, respectively. The propyl fragment of one of the cations and the nitrate group are disordered. During refinement with isotropic displacement parameters, the occupancies of the disordered atoms were refined. These site-occupancy factors were fixed at 0.60 and 0.40 for the major and minor components, respectively. The H atoms of the NH<sub>3</sub> groups and H<sub>2</sub>O molecules were located in difference syntheses and were refined as riding atoms, with N–H = 0.90–0.94 Å and O<sub>water</sub>–H = 0.85–1.10 Å [ $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{N}, \text{O})$ , where  $x = 1.5$  for NH<sub>3</sub> H on atoms N4 and N5, and  $x = 1.2$  for other H]. The remaining H atoms were

positioned geometrically, with C–H = 0.95 and 0.99 Å for methine and methylene H, respectively, and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for methine and methylene H.

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*.

## References

- Aghabozorg, H., Akbari Saei, A. & Ramezanipour, F. (2005). *Acta Cryst.* **E61**, o3242–o3244.
- Aghabozorg, H., Ghadermazi, M. & Ramezanipour, F. (2006). *Acta Cryst.* **E62**, o1143–o1146.
- Brouca-Cabarrecq, C., Fernandes, A., Jaud, J. & Costes, J. P. (2002). *Inorg. Chim. Acta*, **332**, 54–60.
- Bruker (1998). *SAINT-Plus* (Version 6.01) and *SMART* (Version 5.059). Bruker AXS, Madison, Wisconsin, USA.
- Ghosh, S. K. & Bharadwaj, P. K. (2004). *Inorg. Chem.* **43**, 2293–2298.
- Ghosh, S. K. & Bharadwaj, P. K. (2005). *Inorg. Chem.* **44**, 3156–3161.
- Lü, J., Shen, E., Li, Y., Xiao, D., Wang, E. & Xu, L. (2005). *Cryst. Growth Des.* **5**, 65–67.
- Moghimi, A., Ranjbar, M., Aghabozorg, H., Jalali, F., Shamsipur, M. & Chadha, R. K. (2002). *Can. J. Chem.* **80**, 1687–1696.
- Sheldrick, G. M. (1998). *SADABS* (Version 2.01) and *SHELXTL* (Version 5.10). Bruker AXS, Madison, Wisconsin, USA.
- Sheshmani, S., Dalir-Kheirollahi, P., Aghabozorg, H., Shokrollahi, A., Kickelbick, G., Shamsipur, M., Ramezanipour, F. & Moghimi, A. (2005). *Z. Anorg. Allg. Chem.* **631**, 3058–3065.