Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

A polymeric cerium(III) complex of dipicolinic acid

Nobuo Okabe,* Hasuyo Kyoyama and Ayumi Fujimoto

Faculty of Pharmaceutical Sciences, Kinki University, Kowakae 3-4-1, Higashiosaka, Osaka 577-8502, Japan

Correspondence e-mail: okabe@phar.kindai.ac.jp

Received 14 June 2002
Accepted 17 June 2002
Online 21 June 2002

Key indicators

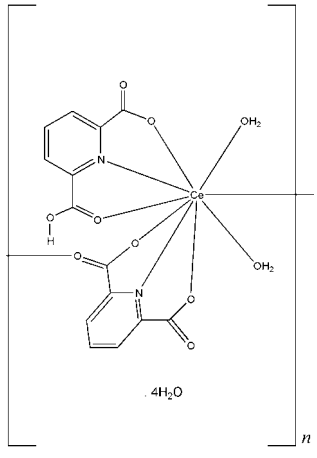
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.014 Å
R factor = 0.055
wR factor = 0.243
Data-to-parameter ratio = 16.6

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

The title compound, *catena*-poly[[[diaqua(6-carboxypyridine-2-carboxylato-*O,N,O′*)cerium(III)]-μ-(pyridine-2,6-dicarboxylato-*O,N,O′:O″*)] tetrahydrate], $[Ce^{III}(C_7H_4NO_4)(C_7H_3NO_4)(H_2O)_2]\cdot 4H_2O$, is a polymeric complex, in which Ce^{III} ions are linked by carboxylate O atoms of the ligands. Each Ce is coordinated by two *N,O,O′*-tridentate dipicolinate ligands, one of which is monoprotonated, and by two O atoms of water molecules. The coordination number of Ce is nine, because of the additional bridging Ce—O bond formed by one ligand.

Comment

Dipicolinic acid (dipic or pyridine-2,6-dicarboxylic acid), a component of bacterial spores (Powell, 1953), has biological activity and induces apotosis in leukemia HL-60 cells (Ogata *et al.*, 2000). The crystal structures of complexes of dipicolinic acid with many divalent and monovalent metal ions have been determined; however, little is known about complexes with the rare earth metals. For this reason, we aimed to determine the structures of lanthanum(III) and cerium(III) complexes of dipicolinic acid, since these metals have the same biological activity, inducing aggregation of human erythrocyte membrane proteins (Du *et al.*, 2001). In a previous study, the structure of the La^{III} complex was determined (Okabe & Kyoyama, 2002). Now the structure of the Ce^{III} complex, (I), has also been determined.



(I)

The structure of (I) is shown in Fig. 1. It is a polymeric chain structure, with a repeat unit consisting of the coordination complex $[Ce(dipic)(Hdipic)(H_2O)_2]$, in which the central Ce atom is bonded to four O atoms and two N atoms of the two *N,O,O′*-tridentate dipicolinates and two O atoms of the water

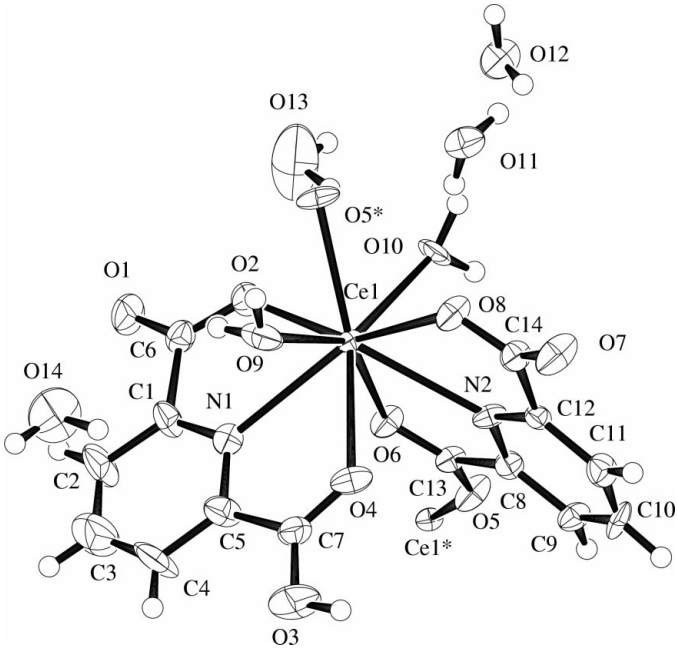


Figure 1
The molecular structure of (I) with the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level. Links to the next asymmetric units in the polymeric chain are shown as Ce1* and O5*.

molecules. The Ce ions in the repeat units are linked together by the carboxylate O atom of the dianionic dipicolinate ligand, forming a polymeric chain structure. One of the ligand molecules is dianionic and the other is monoanionic, having one carboxylate group monoprotonated. In the [Ce(dipic)(Hdipic)] unit, Ce has ninefold coordination, with an overall coordination geometry essentially the same as that of the La^{III} complex. Selected geometric parameters are listed in Table 1.

Experimental

Yellow prismatic crystals were obtained by slow evaporation from a 70% ethanol–water solution of dipicolinic acid (pyridine-2-carboxylic acid) and $CeCl_3·7H_2O$ (1:1 molar ratio).

Crystal data

$[Ce(C_7H_4NO_4)(C_7H_3NO_4)(H_2O)_2]·4H_2O$
M_r = 579.43
Monoclinic, $P2_1/a$
a = 12.983 (4) Å
b = 11.231 (3) Å
c = 14.151 (4) Å
β = 101.76 (2)°
V = 2020.1 (10) Å^3
Z = 4
D_x = 1.905 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 14.9–15.0°
μ = 2.33 mm^{-1}
T = 296.2 K
Prism, yellow
0.50 × 0.50 × 0.50 mm

Data collection

Rigaku AFC-5R diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.196, T_{max} = 0.312
5095 measured reflections
4648 independent reflections
3689 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 27.5°
$h = -16 \rightarrow 0$
$k = 0 \rightarrow 14$
$l = -18 \rightarrow 18$
3 standard reflections
every 150 reflections
intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.243
S = 1.46
4648 reflections
280 parameters
H-atom parameters either not refined or constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.31 e Å^{-3}
$\Delta\rho_{min}$ = −2.27 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ce1—O2	2.480 (7)	N1—C1	1.33 (1)
Ce1—O4	2.556 (7)	N1—C5	1.34 (1)
Ce1—O5^{i}	2.495 (7)	N2—C8	1.34 (1)
Ce1—O6	2.548 (7)	N2—C12	1.36 (1)
Ce1—O8	2.520 (7)	C1—C2	1.36 (2)
Ce1—O9	2.510 (7)	C1—C6	1.53 (1)
Ce1—O10	2.498 (7)	C2—C3	1.36 (2)
Ce1—N1	2.631 (9)	C3—C4	1.34 (2)
Ce1—N2	2.625 (7)	C4—C5	1.37 (2)
O1—C6	1.24 (1)	C5—C7	1.51 (1)
O2—C6	1.29 (1)	C8—C9	1.37 (1)
O3—C7	1.28 (1)	C8—C13	1.51 (1)
O4—C7	1.27 (1)	C9—C10	1.35 (1)
O5—C13	1.26 (1)	C10—C11	1.39 (1)
O6—C13	1.244 (10)	C11—C12	1.38 (1)
O7—C14	1.23 (1)	C12—C14	1.53 (1)
O8—C14	1.28 (1)		
O2—Ce1—O4	123.3 (2)	O5^{i}—Ce1—N1	117.7 (2)
O2—Ce1—O5^{i}	74.7 (2)	O5^{i}—Ce1—N2	130.4 (2)
O2—Ce1—O6	76.4 (2)	O6—Ce1—O8	121.2 (2)
O2—Ce1—O8	153.0 (2)	O6—Ce1—O9	145.2 (2)
O2—Ce1—O9	97.9 (2)	O6—Ce1—O10	72.3 (2)
O2—Ce1—O10	80.5 (2)	O6—Ce1—N1	73.6 (2)
O2—Ce1—N1	61.9 (2)	O6—Ce1—N2	60.2 (2)
O2—Ce1—N2	135.1 (2)	O8—Ce1—O9	78.7 (2)
O4—Ce1—O5^{i}	139.7 (2)	O8—Ce1—O10	85.8 (2)
O4—Ce1—O6	83.2 (2)	O8—Ce1—N1	139.1 (2)
O4—Ce1—O8	81.3 (2)	O8—Ce1—N2	61.7 (2)
O4—Ce1—O9	71.3 (2)	O9—Ce1—O10	141.4 (3)
O4—Ce1—O10	140.9 (2)	O9—Ce1—N1	73.6 (2)
O4—Ce1—N1	61.7 (2)	O9—Ce1—N2	124.1 (2)
O4—Ce1—N2	65.4 (2)	O10—Ce1—N1	133.9 (2)
O5^{i}—Ce1—O6	136.9 (2)	O10—Ce1—N2	76.0 (2)
O5^{i}—Ce1—O8	79.0 (2)	N1—Ce1—N2	111.8 (2)
O5^{i}—Ce1—O9	70.6 (2)	Ce1—O2—C6	126.8 (6)
O5^{i}—Ce1—O10	71.9 (2)		

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

H atoms were located in difference Fourier maps, and were included in the refinement in a riding-model approximation. The H atoms of the water molecules were held fixed.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation & Rigaku, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku Corporation, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997) and *DIRDIF*94 (Beurskens *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

References

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., de Gelder, R., Israel, R. & Smits, J. M. M. (1994). *The DIRDIF*94 *Program System*. Technical Report, Crystallography Laboratory, University of Nijmegen, The Netherlands.

Du, X., Zhang, T., Li, R. & Wang, K. (2001). *J. Inorg. Biochem.* **84**, 67–75.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation & Rigaku (1999). *MSC/AFC Diffractometer Control Software* and *TEXSAN* (Version 1.10). MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Ogata, S., Takeuchi, M., Fujita, H., Shibata, K., Okumura, K. & Taguchi, H. (2000). *Biosci. Biotechnol. Biochem.* **64**, 327–332.
Okabe, N. & Kyoyama, H (2002). *Acta Cryst.* E**58**, m226–m227.
Powell, J. F. (1953). *Biochem. J.* 54, 205–209.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.