

Tetrabutylammonium tetrakis(nitrato- κ^2O,O')-[1,3,5-tris(pyrazolyl)methane- κ^3N]cerate(III)

Shu-Jian Chen, Yi-Zhi Li, Xue-Tai Chen,* Yu-Jun Shi and Xiao-Zeng You

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

Correspondence e-mail: llyyz@nju.edu.cn

Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.009\text{ \AA}$

R factor = 0.043

wR factor = 0.092

Data-to-parameter ratio = 15.2

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

The title complex, $(\text{Bu}_4\text{N})^+[(\text{HCPz}_3)\text{Ce}(\text{NO}_3)_4]^-$ or $(\text{C}_{16}\text{H}_{36}\text{N})[\text{Ce}(\text{NO}_3)_4(\text{C}_{10}\text{H}_{10}\text{N}_6)]$, which is the first lanthanide(III) complex of tris(pyrazolyl)methane (HCPz₃), is 11-coordinate. The Ce—O and Ce—N bond lengths are in the ranges 2.514 (3)–2.685 (3) and 2.686 (4)–2.761 (4) Å, respectively.

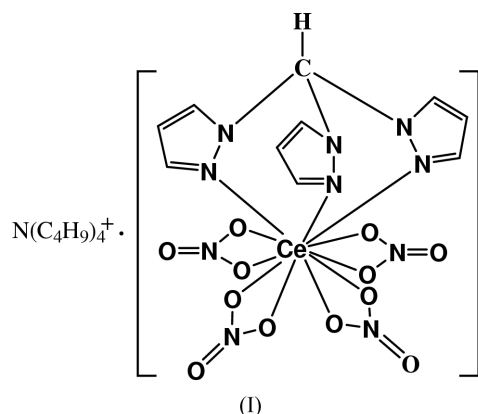
Received 1 November 2002

Accepted 19 November 2002

Online 30 November 2002

Comment

The coordination chemistry of the neutral tripodal ligand tris(pyrazolyl)methane (HCPz₃) is relatively underdeveloped, compared to the anion tris(pyrazolyl)borate (Tp), even though it was introduced by Trofimenko as early as 1986 (Trofimenko, 1986). So far, many transition metal complexes with HCPz₃ have been prepared (Astley *et al.*, 1993; Bhambri & Tocher, 1997; Reger *et al.*, 1996) and reports of main group element complexes have also appeared (Pettinari *et al.*, 1999; Reger *et al.*, 1997). However, no rare earth complexes with this remarkable tridentate ligands have been reported. Herein we report the title Ce^{III} complex, (I).



The crystal structure of (I) consists of discrete $[(\text{HCPz}_3)\text{Ce}(\text{NO}_3)_4]^-$ and Bu_4N^+ ions. The structure of the anion is shown in Fig. 1. The cerium(III) ion is surrounded by three N atoms from the tridentate HCPz₃ ligand and eight O atoms belonging to four bidentate chelating nitrate ligands. This structure is similar to the 11-coordinate Ce–nitrate complexes $\text{Ce}^{\text{III}}(\text{NO}_3)_4(\text{R}_3\text{TPTZ})$ [R is $(\text{CH}_3)_3\text{C}$ and TPTZ is 2,4,6-tris(2-pyridyl)-1,3,5-triazine; Gabriel *et al.*, 1996] and $(\text{Hpy})[\text{Ce}^{\text{IV}}(\text{NO}_3)_4(\text{terpy})]\cdot\text{py}$ (terpy is terpyridine; Grigoriev *et al.*, 2001). The Ce—O bond distances are in the range 2.514 (3)–2.685 (3) Å, and the shortest and longest Ce—O distances are slightly shorter than those in $\text{Ce}^{\text{III}}(\text{NO}_3)_4(\text{R}_3\text{TPTZ})$ [Ce—O 2.522 (7)–2.699 (9) Å] and $(\text{Hpy})[\text{Ce}^{\text{IV}}(\text{NO}_3)_4(\text{terpy})]\cdot\text{py}$ [Ce—O 2.570 (2)–2.709 (2)°].

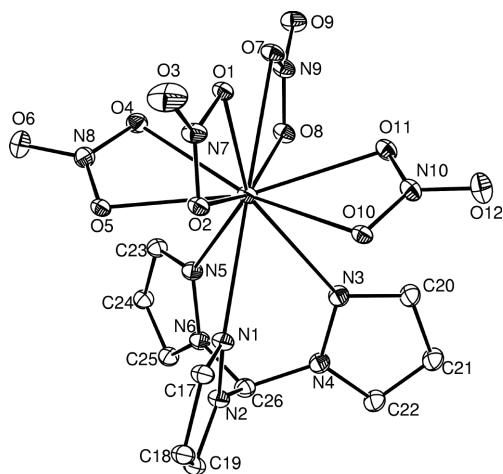


Figure 1
View of the $[(\text{HCPz}_3)\text{Ce}(\text{NO}_3)_4]^-$ anion, with displacement ellipsoids at the 20% probability level.

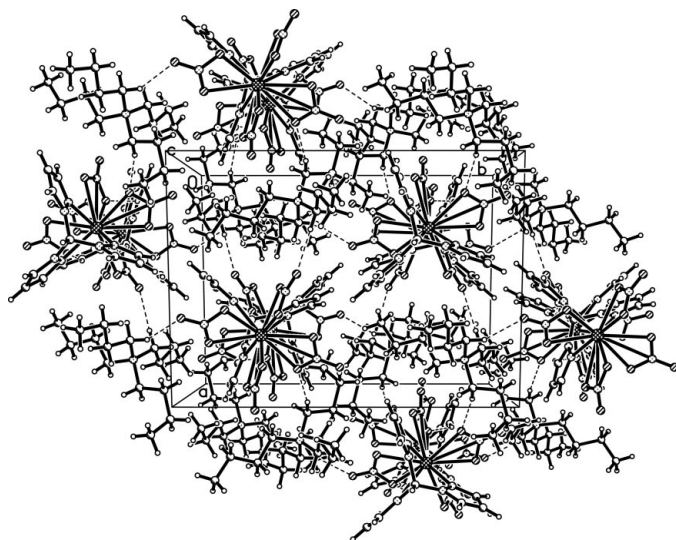


Figure 2
The crystal packing of compound (I), viewed along the c axis, showing $\text{C}-\text{H}\cdots\text{O}$ short contacts.

They are also comparable to those in ten-coordinate Ce^{III} complexes, for example $[(\text{C}_6\text{H}_5)_3\text{C}_2\text{H}_5\text{P}]_2\text{Ce}(\text{NO}_3)_5$ [mean 2.57 (3) Å; Al-Karaghoulis & Wood, 1973] and $[\text{Ce}(\text{ntb})(\text{NO}_3)_3]\cdot\text{H}_2\text{O}$ [ntb is tris(benzimidazol-2-ylmethyl)-amine; mean 2.597 (2) Å; Su *et al.*, 1998]. The nitrate ligands are coordinated to the cerium(III) ion in a slightly asymmetrical manner, with differences in the $\text{Ce}\cdots\text{O}$ distances of 0.176 (2), 0.022 (2), 0.065 (2) and 0.065 (2) Å for the individual nitrate groups. Ce^{III} is approximately coplanar with each of the nitrate ligands. The average dihedral angle of the chelating nitrate ligands is 48°; *viz.* the dihedral angles are between planes 1 (O1/O2/O3/N7) and 2 (O4/O5/O6/N8), and between planes 1 and 3 (O7/O8/O9/N9). The $\text{Ce}^{\text{III}}-\text{N}$ distances are in the range 2.686 (4)–2.761 (4) Å; however, the shortest and longest $\text{Ce}-\text{N}$ distances are slightly longer than those in

$\text{Ce}^{\text{III}}(\text{NO}_3)_4(\text{R}_3\text{TPTZ})$ [$\text{Ce}-\text{N}$ 2.673 (7)–2.734 (7) Å] and $(\text{Hpy})[\text{Ce}^{\text{IV}}(\text{NO}_3)_4(\text{terpy})]\cdot\text{py}$ [$\text{Ce}-\text{N}$ 2.624 (2)–2.706 (2) Å]. The three angles (N1–Ce1–N3, N1–Ce1–N5 and N3–Ce1–N5) of the tridentate ligand of the title complex are in the range 63.53 (13)–70.10 (13)°, and are larger than those of $\text{Ce}^{\text{III}}(\text{NO}_3)_4(\text{R}_3\text{TPTZ})$ [dihedral angles 59.4 (2)–62.4 (2)°] and $(\text{Hpy})[\text{Ce}^{\text{IV}}(\text{NO}_3)_4(\text{terpy})]\cdot\text{py}$ [dihedral angles 57.68 (7)–61.37 (7)°]. There are intermolecular $\text{C}-\text{H}\cdots\text{O}$ close contacts leading to a three-dimensional polymeric network (Fig. 2 and Table 2).

Experimental

All the chemicals used are commercially available, except for HCPz_3 , which was prepared according to the literature method of Reger (2000). Elemental analyses were carried out on a Perkin–Elmer 240 C elemental analyser. To an ethanol (25 ml) solution containing $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (0.5 mmol) was added, stepwise, HCPz_3 (0.5 mmol) and ${}^n\text{Bu}_4\text{NBr}$ (0.5 mmol), and the reaction mixture refluxed for 30 min with stirring and then filtered. The filtrate was allowed to stand in air for several days, producing colorless rod-like crystals of (I) (yield *ca* 70%). Analysis calculated: C 36.96, H 5.49, N 18.24%; found: C 36.91, H 5.55, N 18.28%. ${}^1\text{H}$ NMR (500 MHz, DMSO): δ (p.p.m.) 7.89 and 7.66 (*d, d*, 3H, 3H, 3-H and 5-H on Pz), 6.42 (*t*, 3H, 4H on Pz), 8.97 (*s*, 1H on HCPz_3), 3.16 and 0.93 (*t, t*, 8H, 8H, CH_2 and CH_3 on ${}^n\text{Bu}^4\text{N}$), 1.56 and 1.30 (*m, m*, 8H, 8H, CH_2 and CH_2 on ${}^n\text{Bu}^4\text{N}$).

Crystal data

$(\text{C}_{16}\text{H}_{36}\text{N})[\text{Ce}(\text{NO}_3)_4(\text{C}_{10}\text{H}_{10}\text{N}_6)]$
 $M_r = 844.86$
 Monoclinic, $P2_1/c$
 $a = 12.484$ (1) Å
 $b = 16.742$ (1) Å
 $c = 18.267$ (1) Å
 $\beta = 102.82$ (1)°
 $V = 3722.8$ (4) Å³
 $Z = 4$

$D_x = 1.507$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4597 reflections
 $\theta = 2.2$ –23.8°
 $\mu = 1.29$ mm⁻¹
 $T = 293$ (2) K
 Rod, colorless
 $0.3 \times 0.2 \times 0.2$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\text{min}} = 0.740$, $T_{\text{max}} = 0.771$
 18 988 measured reflections

6546 independent reflections
 4018 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -14 \rightarrow 14$
 $k = 0 \rightarrow 19$
 $l = 0 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.092$
 $S = 1.02$
 6546 reflections
 431 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 1.99P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.67$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.59$ e Å⁻³

Table 1

Selected interatomic distances (Å).

Ce1–O1	2.514 (3)	Ce1–O7	2.660 (3)
Ce1–O11	2.572 (3)	Ce1–O2	2.685 (3)
Ce1–O5	2.602 (3)	Ce1–N1	2.686 (4)
Ce1–O8	2.615 (3)	Ce1–N5	2.705 (4)
Ce1–O4	2.626 (3)	Ce1–N3	2.761 (4)
Ce1–O10	2.630 (3)		

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C4—H4B···O9 ⁱ	0.97	2.46	3.421 (7)	173
C5—H5B···O12 ⁱⁱ	0.97	2.55	3.445 (8)	153
C13—H13A···O5 ⁱⁱⁱ	0.97	2.37	3.311 (7)	163
C19—H19···O1 ^{iv}	0.93	2.31	3.080 (6)	140
C25—H25···O11 ^{iv}	0.93	2.49	3.365 (6)	158
C26—H26···O7 ^{iv}	0.98	2.25	3.221 (6)	170

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

The H atoms were positioned geometrically and refined with a riding model.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported by a Natural Science Grant of Jiangsu Province (BK 99032). We also thank the Nanjing

University Talent Development Foundation for a research grant (No. 0205005122).

References

- Al-Karaghoul, A. R. & Wood, J. S. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2318–2321.
- Astley, T., Gulbis, J. M., Hitchman, M. A. & Tiekink, E. R. T. (1993). *J. Chem. Soc. Dalton Trans.* pp. 509–515.
- Bhambri, S. & Tocher, D. A. (1997). *J. Chem. Soc. Dalton Trans.* pp. 3367–3372.
- Bruker (2000). *SMART, SAINT, SADABS and SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Gabriel, Y. S. C., Drew, M. G. B., Hudson, M. J., Isaacs, N. S. & Byers, P. (1996). *Polyhedron*, **15**, 3385–3398.
- Grigoriev, M. S., Auwer, C. D. & Madic, C. (2001). *Acta Cryst.* **C57**, 1141–1143.
- Pettinari, C., Pellei, M., Cingolani, A., Martini, D., Drozdov, A., Troyanov, S., Panzeri, W. & Mele, A. (1999). *Inorg. Chem.* **38**, 5777–5787.
- Reger, D. L., Collins, J. E., Myers, S. M., Rheingold, A. L. & Liable-Sands, L. M. (1996). *Inorg. Chem.* **35**, 4904–4909.
- Reger, D. L., Collins, J. E., Rheingold, A. L., Liable-Sands, L. M. & Yap, G. P. A. (1997). *Inorg. Chem.* **36**, 345–351.
- Reger, D. L., Grattan, T. C., Brown, K. J., Little, C. A., Lamba, J. J. S., Rheingold, A. L. & Sommer, R. D. (2000). *J. Organomet. Chem.* **607**, 120–128.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Su, C.-Y., Kang, B.-S., Mu, X.-Q., Sun, J., Tong, Y.-X. & Chen, Z.-N. (1998). *Aust. J. Chem.* **51**, 565–571.
- Trofimenko, S. (1986). *Prog. Inorg. Chem.* **34**, 115.