Trinitratobis{N'-[1-(2-pyridyl)-ethylidene]isonicotinohydrazide}-cerium(III): a three-dimensional cerium–organic supramolecular structure

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The Ce^{III} ion in the title complex, $[Ce(NO_3)_3(C_{13}H_{12}N_4O)_2]$, is 12-coordinated by six chelating nitrate O atoms and six donors (2 O and 4 N atoms) of two N'-[1-(2-pyridyl)ethylidene]-isonicotinohydrazide ligands, exhibiting a bicapped penta-gonal-antiprism-type coordination geometry. The title complex possesses C_2 point symmetry and is located on a twofold crystallographic axis. Each molecule is linked with four surrounding molecules by four N—H···N hydrogen bonds, resulting in an extended two-dimensional layer parallel to the ab plane, while π–π interactions between pyridine rings from neighboring complex molecules connect the two-dimensional layers into a three-dimensional cerium–organic supramolecular structure.

Comment

Lanthanide complexes have been widely studied because they exhibit a range of different coordination numbers and coordination configurations. Numerous nitrate-containing lanthanide complexes are archived in the Cambridge Structural Database (Version 5.30 of November 2008; Allen, 2002). A large variation in the coordination number and coordination configuration of the metal atom for these lanthanide nitrate complexes is reported. Examples of eight-coordinate lanthanide complexes with nitrate groups are $[Nd(C_{13}H_{12}-OP)_2(C_7H_7N)(NO_3)](NO_3)_2$·4EtOH (Gan et al., 2003) and $[Dy(L)(NO_3)\{(CH_3)_2SO\}]$ (L = 2,6-diacetylpyridinebisben-zoylhydrazone; Tamboura et al., 2003). Lanthanide nitrate complexes with coordination number 9 have also been reported (Platas et al., 1999; Fukuda et al., 2002; Tamboura et al., 2003; Hudson et al., 2003; Diamantopoulou et al., 2003; Drew et al., 2004; Lu et al., 2004; Dröse & Gottfriedsen, 2008). Ten-coordinate lanthanide nitrate complexes include $[La(NO_3)_3(CH_3CN)_4]$, $[La(NO_3)_3(CH_3CN)_3(H_2O)]$, $[La-$

$(NO_3)_3(terpy)(CH_3CN)]$, $[La(NO_3)_3(terpy)(H_2O)]$ (terpy is 2,2';6',2''-terpyridine; Fréchette & Bensimon, 1995), [Ln(ter-py)(acac)(NO_3)_2(H_2O)] (acac is acetylacetonate; Fukuda et al., 2002), $[Cu_2Gd(L)_2(NO_3)_2(MeOH)_2]NO_3$·MeOH [$L$ is 2,6-di(acetoacetyl)pyridine; Shiga et al., 2003] and $[Ce(NO_3)_3-(phen)_2]$ (phen is 1,10-phenanthroline; Lin & Feng, 2003). Typical 11-coordinate lanthanide nitrate complexes are $[La-(NO_3)_4(terpy)(CH_3CN)]^-$, $[La(NO_3)_4(terpy)(H_2O)]^-$ (Fréch-ette & Bensimon, 1995), $(H_2terpy)[Sm(terpy)(NO_3)_4]NO_3$ (Drew et al., 1998) and $(C_5H_6N)[Ce(NO_3)_4(terpy)]$·$C_5H_5N$ (Grigoriev et al., 2001). We report here the structure of a 12-coordinate cerium nitrate complex with N'-[1-(2-pyridyl)-ethylidene]isonicotinohydrazide, (I) (Fig. 1).

(I)
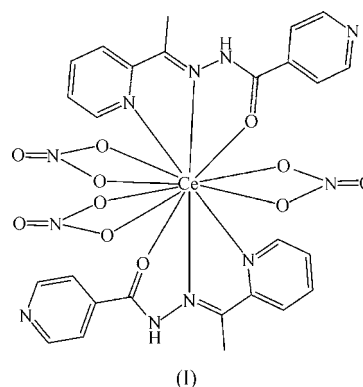
The molecule of (I) exhibits C_2 point symmetry, with atoms Ce1, N6 and O6 located on a crystallographic twofold rotation axis. The Ce^{3+} ion is coordinated by 12 donors (Fig. 2), of which atoms O2, O3, O2^i, O3^i, O5 and O5^i [symmetry code: (i) $-x, y, -z + \frac{1}{2}$] are from three bidentate nitrate groups; two carbonyl O atoms (O1 and O1^i) and four N atoms (N1, N2, N1^i and N2^i) from two symmetry-related N'-[1-(2-pyridyl)ethyl-
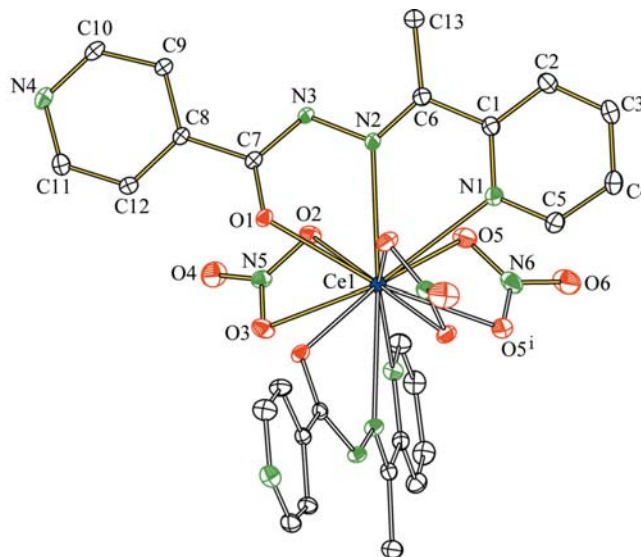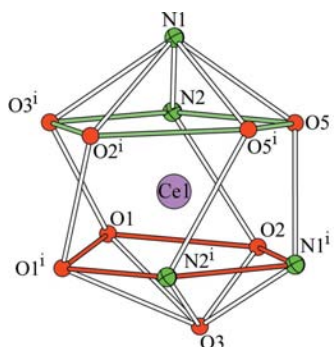

Figure 1
The molecular structure of complex (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.]

idene]isonicotinohydrazide ligands complete the coordination. The environment around the Ce1 atom can be described as a bicapped pentagonal antiprism with atoms O3^i, O2^i, O5^i, O5 and N2, and atoms O1, O2, N1^i, N2^i and O1^i forming the two pentagonal bases, atom N1 of the pyridine group and atom O3 of a coordinated nitrate group being the two capping atoms. The dihedral angle between the two pentagonal bases is 4.11 (9)°. The Ce—O(NO$_3$) bond distances in the title complex range from 2.620 (2) to 2.684 (2) Å, with a mean value of 2.642 Å (Table 1). The corresponding mean values in the 12-coordinate compound [Ce(NO$_3$)$_3$(C$_{13}$H$_{11}$N$_3$O)$_2$]·C$_3$H$_6$O·2H$_2$O (Christidis *et al.*, 1999), the 11-coordinate complex Ce(NO$_3$)$_4$(*L*) and the ten-coordinate 2[LH$_3$]$^{3+}$·[Ce(NO$_3$)$_5$(OH$_2$)]$^-$·[Ce(NO$_3$)$_5$(EtO)]$^{2-}$·2NO$_3^-$·OH$^-$ (*L* = 2,4,6-tri-*tert*-butylpyridine-1,3,5-triazine; Chan *et al.*, 1996) are 2.675, 2.599 and 2.595 Å, respectively. This indicates that the Ce—O(NO$_3$) bond distance gets longer with higher coordination number. The Ce—O(carbonyl) bond distance in (I) is 2.603 (2) Å. This indicates that the Ce—O(carbonyl) bond is slightly stronger than the Ce—O(NO$_3$) bonds in the title complex. This was also observed in other lanthanide complexes (Shiga *et al.*, 2003; Fukuda *et al.*, 2002; Tamboura *et al.*, 2003).

The three nitrate groups are essentially planar; two are related by a twofold rotation axis, while the third (N6/O5/O5^i/O6) exhibits C_2 symmetry. The two hydrazone ligands are close to being coplanar. The dihedral angle between the two pyridine rings in the same hydrazone ligand is 6.5 (2)°. The two hydrazone ligands are related by the twofold rotation axis; the dihedral angles between the two corresponding pyridine rings in the two symmetry-related hydrazone ligands are 84.20 (9) and 82.80 (9)°, respectively.

As illustrated in Fig. 3, every cerium complex molecule connects four adjacent complex molecules *via* four N—H···N hydrogen bonds [N3—H3*B*···N4^{ii}, N3^{iii}—H3*B*^{iii}···N4, N3^i—H3*B*^{i}···N4^{iv} and N3^v—H3*B*^{v}···N4^i; symmetry codes: (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x-\frac{1}{2}, y+\frac{1}{2}, z$; (iv) $x-\frac{1}{2}, y-\frac{1}{2}, z$; Table 2] to give an extended two-dimensional layer parallel to the *ab* plane.

The N1/C1–C5 pyridine ring in the molecule at (x, y, z) and the N4/C8–C12 pyridine ring of the molecule at ($-x, -y, -z$) are almost parallel, with a dihedral angle of 6.5 (2)° between

them. The interplanar spacing is about 3.503 Å and the ring-centroid separation is 3.680 (2) Å. This indicates a π–π interaction (shown as dashed lines in Fig. 4) between the two pyridine rings, resulting in an extended one-dimensional chain along the *c* axis and linking the two-dimensional layers into a three-dimensional metal–organic supramolecular network.

Up to now, the highest coordination number in the known lanthanide nitrate complexes is 12. It is worth noting that almost all of the lanthanide nitrate complexes with coordination number 12 contain one of the La^{3+} or Ce^{3+} lanthanide ions. This may be because La^{3+} and Ce^{3+} ions possess a $4f^{n-1}5d^16s^2$ electronic configuration. This type of complex possesses the structural units Ln(NO$_3$)$_6$ or Ln(*L*)$_m$(NO$_3$)$_3$ (where m = 1 or 2). Examples of complexes with the structural unit Ln(NO$_3$)$_6$ are [bis(8-quinolyloxyethyl) ether·H$_3$O]$_3$[La(NO$_3$)$_6$] (Tang *et al.*, 1996), 3[H$_2$terpy]$^{2+}$·2[La(NO$_3$)$_6$]$^{3-}$·3H$_2$O (Drew *et al.*, 1998) and [Me$_4$cyclam(OHO)$_2$]$_2$[Ln(NO$_3$)$_6$](NO$_3$)·H$_2$O (cyclam is 1,4,8,11-tetraazacyclotetradecane; Lu *et al.*, 2004). Examples of complexes with the structural unit Ln(*L*)$_m$(NO$_3$)$_3$ are [Ce(NO$_3$)$_3$(C$_{15}$H$_{11}$N$_3$)(CH$_4$O)$_2$] (Grigoriev *et al.*, 2001), [La(NO$_3$)$_3$L] (*L* is 1,9-diaza-18-crown-6; Shestakova *et al.*, 2001) and [La(NO$_3$)$_3$(C$_6$H$_{14}$O$_6$)]·4H$_2$O (Su *et al.*, 2007).

Describing the coordination polyhedra of the lanthanide atoms in the 12-coordinate complexes is quite difficult. An irregular icosahedron is the ambiguous interpretation in some publications concerning these complexes. The coordination geometry of the Ce atom in (I) is a bicapped pentagonal antiprism. All known lanthanide nitrate complexes with coordination number 12 have a discrete structure.

Figure 3
The extended two-dimensional network of complex (I), parallel to the *ab* plane, formed by N—H···N hydrogen bonds.

Figure 4
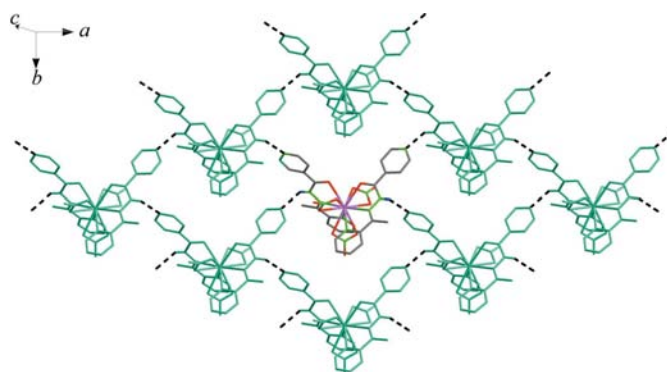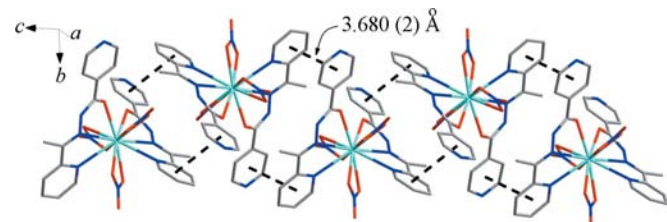The one-dimensional chain along the *c* axis, formed by π–π stacking.

Figure 2
The coordination geometry of the bicapped pentagonal antiprism for the Ce atom in (I). [Symmetry code: (i) $-x, y, -z+\frac{1}{2}$.]

The IR spectrum of the title complex exhibits two bands at 3391 and 1635 cm^{-1} due to ν(NH) and ν(C=O) stretches, respectively. They show the existence of the NH group in the hydrazone ligand, which means that the hydrazone group in complex (I) behaves as a neutral ligand and coordinates to the Ce ion in the keto form *via* the carbonyl O, hydrazine N and pyridine N atoms.

The absorption bands at 1479, 1316 and 1037 cm^{-1} are assigned to the ν(N=O) (ν_1), ν_{asym}(NO$_2$) (ν_5) and ν_{sym}(NO$_2$) (ν_2) vibrations, respectively, of the chelating bidentate nitrate ion (Aruna & Alexander, 1996). The larger separation of 163 cm^{-1} between the two highest-frequency bands (ν_1 and ν_5) indicates strong interaction of the O atoms of the nitrate group with the lanthanide ions and is typical of bidentate coordination. The bands observed at 1595 and 1550 cm^{-1} are assigned to the ν(C=N) vibration (Jagst *et al.*, 2005). The band due to the ν(N—N) mode appears at 1009 cm^{-1} (Tamboura *et al.*, 2004). These are consistent with the crystal structure of (I).

Thermogravimetric analysis of complex (I) shows unique weight losses between 510 and 514 K to give a loss of 83.9%, corresponding to the loss of two hydrazone ligands and three nitrate ions per formula unit. The product of thermal decomposition is Ce$_2$O$_3$. Compared with the high thermal stability of most of lanthanide nitrate complexes (Aruna & Alexander, 1996), the thermal stability of the title lanthanide nitrate complex is quite low.

Experimental

N'-[1-(2-Pyridyl)ethylidene]isonicotinohydrazide (25 mg, 0.10 mmol) was added to a solution of Ce(NO$_3$)$_3$·6H$_2$O (44 mg, 0.10 mmol) in a mixed solvent of dry methanol and DMF (1:1 *v/v*, 10 ml) with stirring. After stirring for 30 min, the reaction mixture was filtered and left to stand at room temperature. Yellow prism-shaped crystals suitable for X-ray diffraction were obtained by slow evaporation after 10 d (yield 58%). Analysis found: C 38.59, H 3.07, N 19.18%; calculated for C$_{26}$H$_{24}$CeN$_{11}$O$_{11}$: C 38.71, H 3.00, N 19.10%.

Crystal data

[Ce(NO$_3$)$_3$(C$_{13}$H$_{12}$N$_4$O)$_2$]
M_r = 806.68
Monoclinic, $C2/c$
a = 21.842 (11) Å
b = 10.591 (4) Å
c = 15.105 (5) Å
β = 122.317 (15)°

V = 2953 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.62 mm^{-1}
T = 293 K
0.28 × 0.17 × 0.15 mm

Data collection

Rigaku Weissenberg IP diffractometer
Absorption correction: multi-scan (*TEXRAY*; Molecular Structure Corporation, 1999)
T_{min} = 0.686, T_{max} = 1.000 (expected range = 0.538–0.784)

14241 measured reflections
3384 independent reflections
3226 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.060
S = 1.13
3384 reflections

224 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.68 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ce1—O1	2.6032 (17)	Ce1—O3	2.684 (2)
Ce1—O2	2.620 (2)	Ce1—N2	2.734 (2)
Ce1—O5	2.621 (2)	Ce1—N1	2.904 (2)
O1^i—Ce1—O1	67.12 (7)	O5—Ce1—N2	73.11 (6)
O1—Ce1—O2	66.21 (6)	O3—Ce1—N2	107.34 (7)
O1—Ce1—O2^i	114.00 (6)	O1—Ce1—N2^i	117.54 (6)
O2—Ce1—O2^i	179.78 (8)	O2—Ce1—N2^i	110.70 (6)
O1—Ce1—O5	122.32 (6)	O5—Ce1—N2^i	111.19 (6)
O2—Ce1—O5	69.21 (7)	O3—Ce1—N2^i	70.55 (7)
O1—Ce1—O5^i	169.34 (6)	N2—Ce1—N2^i	175.54 (8)
O2—Ce1—O5^i	110.58 (7)	O1—Ce1—N1^i	123.93 (6)
O5—Ce1—O5^i	48.87 (10)	O2—Ce1—N1^i	67.18 (6)
O1—Ce1—O3^i	71.12 (6)	O5—Ce1—N1^i	64.08 (6)
O2—Ce1—O3^i	132.21 (6)	O3—Ce1—N1^i	61.03 (7)
O5—Ce1—O3^i	121.14 (7)	N2—Ce1—N1^i	126.90 (7)
O1—Ce1—O3	65.02 (6)	O1—Ce1—N1	107.11 (6)
O2—Ce1—O3	47.93 (6)	O2—Ce1—N1	112.69 (6)
O5—Ce1—O3	107.32 (7)	O5—Ce1—N1	60.38 (7)
O3^i—Ce1—O3	126.84 (9)	O3—Ce1—N1	160.40 (6)
O1—Ce1—N2	58.18 (6)	N2—Ce1—N1	55.90 (6)
O2—Ce1—N2	69.31 (6)	N1^i—Ce1—N1	118.48 (9)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3B···N4^{ii}	0.86	2.27	2.905 (3)	131

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

All H atoms were placed in calculated positions and refined using a riding model [C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms, C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms, and N—H = 0.86 Å and U_{iso}(H) = 1.2U_{eq}(N)].

Data collection: *TEXRAY* (Molecular Structure Corporation, 1999); cell refinement: *TEXRAY*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS98* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL98* (Sheldrick, 2008); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *SHELXL97/2* (Sheldrick, 2008).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Aruna, V. A. J. & Alexander, V. (1996). *J. Chem. Soc. Dalton Trans.* pp. 1867–1873.

Chan, G. Y. S., Drew, M. G. B., Hudson, M. J., Isaacs, N. S. & Byers, P. (1996). *Polyhedron*, **15**, 3385–3398.

Christidis, P. C., Tossidis, I. A. & Paschalidis, D. G. (1999). *Acta Cryst.* C**55**, 707–710.

Diamantopoulou, E., Papaefstathiou, G. S., Terzis, A., Raptopoulou, C. P., Desseyn, H. O. & Perlepes, S. P. (2003). *Polyhedron*, **22**, 825–835.

Drew, M. G. B., Hill, C., Hudson, M. J., Iveson, P. B., Madic, C. & Youngs, T. G. A. (2004). *Dalton Trans.* pp. 244–251.

metal-organic compounds

Drew, M. G. B., Hudson, M. J., Iveson, P. B., Russell, M. L., Liljenzin, J.-O., Skalberg, M., Spjuth, L. & Madic, C. (1998). *J. Chem. Soc. Dalton Trans.* pp. 2973–2980.

Dröse, P. & Gottfriedsen, J. (2008). *Z. Anorg. Allg. Chem.* **634**, 87–90.

Fréchette, M. & Bensimon, C. (1995). *Inorg. Chem.* **34**, 3520–3527.

Fukuda, Y., Nakao, A. & Hayashi, K. (2002). *J. Chem. Soc. Dalton Trans.* pp. 527–533.

Gan, X.-M., Paine, R. T., Duesler, E. N. & Nöth, H. (2003). *Dalton Trans.* pp. 153–159.

Grigoriev, M. S., Den Auwer, C. & Madic, C. (2001). *Acta Cryst.* C**57**, 1141–1143.

Hudson, M. J., Drew, M. G. B., Foreman, M. R. St J., Hill, C., Huet, N., Madic, C. & Youngs, T. G. A. (2003). *Dalton Trans.* pp. 1675–1685.

Jagst, A., Sanchez, A., Vazquez-Lopez, E. M. & Abram, U. (2005). *Inorg. Chem.* **44**, 5738–5744.

Lin, Q.-Y. & Feng, Y.-L. (2003). *Z. Kristallogr. New Cryst. Struct.* **218**, 531–532.

Lu, W.-J., Zhang, L.-P., Chan, H.-S., Chan, T.-L. & Mak, T. C. W. (2004). *Polyhedron*, **23**, 1089–1096.

McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.

Molecular Structure Corporation (1999). *TEXRAY* (Version 1.10) and *TEXSAN* (Version 1.10). MSC, The Woodlands, Texas, USA.

Platas, C., Avecilla, F., de Blas, A., Geraldes, C. F. G. C., Rodríguez-Blas, T., Adams, H. & Mahía, J. (1999). *Inorg. Chem.* **38**, 3190–3199.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Shestakova, A. K., Chertkov, V. A., Schneider, H.-J. & Lysenko, K. A. (2001). *Org. Lett.* **3**, 325–327.

Shiga, T., Ohba, M. & Ōkawa, H. (2003). *Inorg. Chem. Commun.* **6**, 15–18.

Su, Y.-L., Yang, L.-M., Xu, Y.-Z., Wang, Z.-M., Weng, S.-F., Yan, C.-H., Wang, D.-J. & Wu, J.-H. (2007). *Inorg. Chem.* **46**, 5508–5517.

Tamboura, F. B., Diop, M., Gaye, M., Sall, A. S., Barry, A. H. & Jouini, T. (2003). *Inorg. Chem. Commun.* **6**, 1004–1010.

Tamboura, F. B., Haba, P. M., Gaye, M., Sall, A. S., Barry, A. H. & Jouini, T. (2004). *Polyhedron*, **23**, 1191–1197.

Tang, Y., Feng, Y.-C., Gan, X.-M. & Tan, M.-Y. (1996). *Polyhedron*, **15**, 3219–3223.