Data collection

Delft Instruments FAST TV area-detector diffractometer
ω scans
Absorption correction: none
6191 measured reflections
4062 independent reflections
1723 reflections with $I > 2\sigma(I)$
$R_{int} = 0.070$
$\theta_{max} = 24.88°$
$h = -10 \rightarrow 10$
$k = -15 \rightarrow 9$
$l = -17 \rightarrow 16$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.117$
$S = 0.709$
4062 reflections
346 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.421$ e Å^{-3}
$\Delta\rho_{min} = -0.289$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zr1—N4	2.154 (5)	Zr1—N3	2.168 (6)
Zr1—N1	2.163 (6)	Zr1—Cl1	2.495 (2)
Zr1—N2	2.164 (6)	Zr1—Cl2	2.508 (3)
N4—Zr1—N1	74.2 (2)	N2—Zr1—Cl1	89.68 (17)
N4—Zr1—N2	122.3 (2)	N3—Zr1—Cl1	142.76 (16)
N1—Zr1—N2	77.6 (3)	N4—Zr1—Cl2	88.29 (17)
N4—Zr1—N3	78.5 (2)	N1—Zr1—Cl2	144.20 (19)
N1—Zr1—N3	120.1 (2)	N2—Zr1—Cl2	137.06 (19)
N2—Zr1—N3	74.0 (2)	N3—Zr1—Cl2	85.19 (16)
N4—Zr1—Cl1	136.78 (19)	Cl1—Zr1—Cl2	84.79 (8)
N1—Zr1—Cl1	87.18 (16)		

The temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). Data were collected from 0.2° ω-rotation exposures of 10 s each, with a crystal-to-detector distance of 49.37 (8) mm. Coverage of the unique set was over 74% complete to at least 25° in θ. Crystal decay was found to be negligible by comparison of intensities of repeated reflections. H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached. The disordered THF solvent was modelled as two partially occupied positions with occupancies of 0.25 and with some distance restraints.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1992). Cell refinement: *MADNES*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL97*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher *et al.*, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993). We also wish to thank Professor M. B. Hursthouse and the EPSRC X-ray crystallographic service (University of Wales, Cardiff) for collecting the diffraction data.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1287). Services for accessing these data are described at the back of the journal.

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Bis[*N*-benzoyl-*N*′-(2-pyridylmethylene)hydrazine]trinitratocerium(III) acetone dihydrate†

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Abstract

The crystal structure of the title compound, $[Ce(NO_3)_3(C_{13}H_{11}N_3O)_2]\cdot C_3H_6O\cdot 2H_2O$, has been determined. The Ce^{III} atom is 12-coordinate by linking to two tridentate 2-pyridinecarboxaldehyde benzoylhydrazone ligands and three bidentate nitrate ligands. The Ce—O distances range between 2.528 (3) and 2.759 (4) Å, and the Ce—N distances range between 2.725 (4) and 2.848 (4) Å. All the water molecules are involved in hydrogen-bond formation with the Ce-containing molecules.

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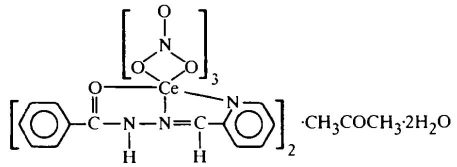
† Alternative name: tris(nitrato-*O*,*O*′)bis{*N*-[(2-pyridyl-*N*)methyleneamino-*N*]benzamide-*O*}cerium(III) acetone dihydrate.

Comment

The asymmetric unit of the title structure, (I), comprises two trinitratobis[*N*-benzoyl-*N*′-(2-pyridylmethylene)hydrazine]$\mathrm{Ce^{III}}$ molecules (TBCE), two acetone molecules and four water molecules (Fig. 1). The



(I)

Ce atom is linked to two tridentate 2-pyridinecarboxaldehyde benzoylhydrazone ligands (PBH) and three bidentate nitrate ligands, giving rise to a total coordination number of 12. The linking of the PBH ligand to the metal atom is accomplished through the pyridine nitrogen, the azomethine nitrogen and the carbonyl oxygen. Thus, two five-membered chelate rings are formed, which together with the pyridine ring constitute an almost planar fused system, the maximum angular deviation of these planes being 13.0 (1) and 13.4 (1)° in the two TBCE molecules.

The coordination polyhedron around the Ce atom is an irregular icosahedron, which may also be described as a very distorted six-capped trigonal antiprism (Fig. 2). The angles formed by the two trigonal bases and the equatorial plane do not exceed 10.9 (2) and 17.8 (2)° in the two TBCE molecules. Moreover, the Ce atom, lying in the equatorial plane, is almost equidistant from the two trigonal bases of the antiprism. Similar coordination geometry was found in other 12-coordinate lanthanides, *e.g.* in cerium magnesium nitrate hydrate (Zaklin *et al.*, 1963), in $[\mathrm{La(NO_3)_3}L^1]$, where L^1 = 2,7,13,18-tetramethyl-3,6,14,17,23,24-hexaazatricyclo-$[17.3.1.1^{8,12}]$tetracosa-1(23),2,6,8,10,12(24),13,17,19,21-decaene (Arif *et al.*, 1987), and in (4,7,13,16-tetraoxa-1,10-diazacyclo-octadecane)tris(nitrato-*O*′)cerium(1,10-diaza-18-crown-6)tris(nitrato-*O*,*O*′)cerium (Fupei *et al.*, 1989). In the two latter compounds, as in the title compound, the two nitrate groups are situated on one side of the mean plane of the organic ligand(s), with the remaining nitrate group on the opposite side. The Ce—O distances range between 2.528 (3) and 2.759 (4), and 2.530 (3) and 2.740 (4) Å in the two TBCE molecules, the respective mean distances being 2.646 (2) and 2.644 (2) Å. Similarly, the Ce—N distances range between 2.725 (4) and 2.848 (4) Å, and 2.731 (4) and 2.838 (4) Å in the two TBCE molecules, the respective mean distances being 2.779 (2) and 2.777 (2) Å. These values are comparable with those found in related compounds, *e.g.* in the last-mentioned Ce complex, where the Ce—O and Ce—N distances are in the ranges 2.633–2.812 and 2.677–2.712 Å, respectively, with respective mean values of 2.698 and 2.695 Å (Fupei *et al.*, 1989). In both TBCE molecules, the benzene and pyridine rings have normal dimensions. All the water molecules are involved in hydrogen-bond formation with the PBH ligands, while the acetone molecules interact only by van der Waals forces with their surrounding molecules.

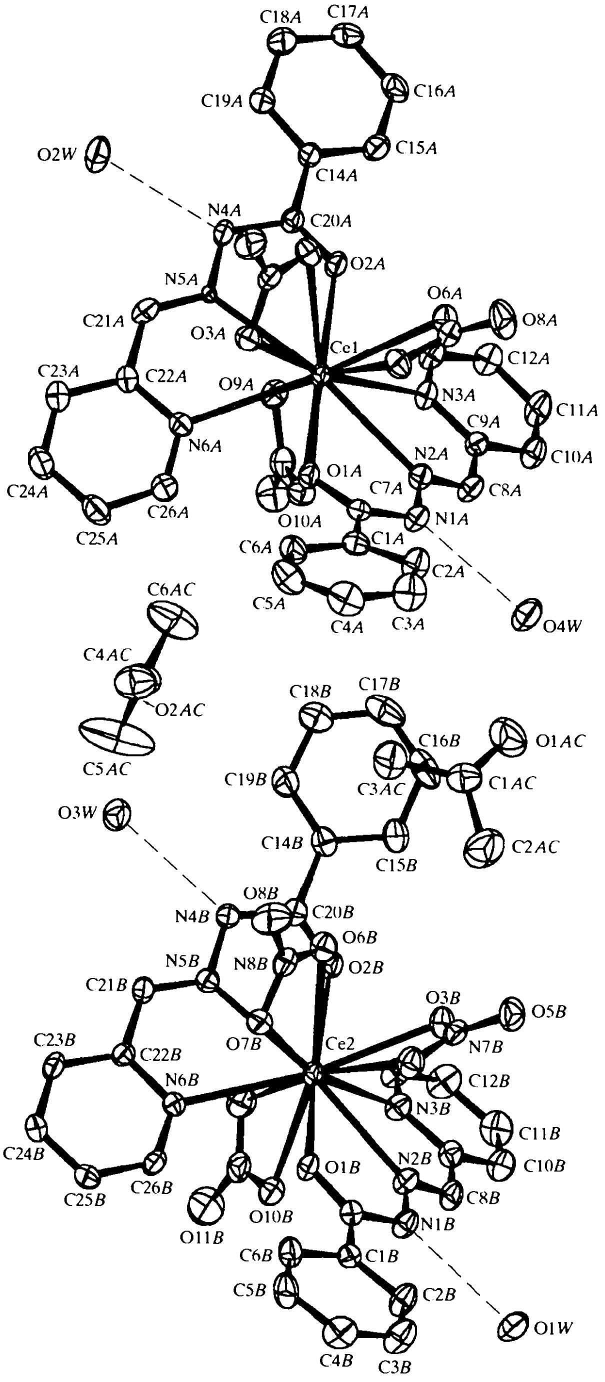


Fig. 1. The asymmetric unit of the title structure showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

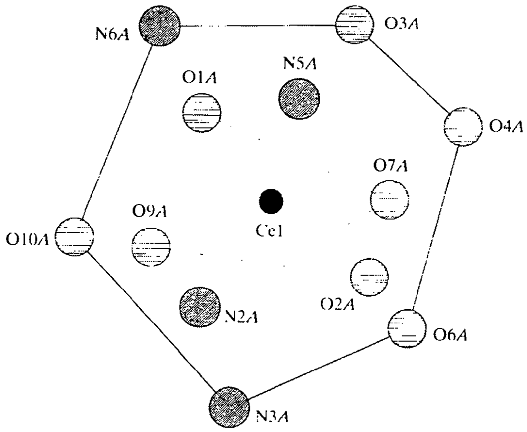


Fig. 2. The coordination polyhedron around the Ce1 atom. The atomic arrangement around the Ce2 atom is similar.

Experimental

The title compound was synthesized by mixing a solution of cerium nitrate hexahydrate (1 mmol) in water (1 ml) with a solution of the ligand (2 mmol) in acetone (20 ml). The mixture was kept in the refrigerator and thin needle-shaped yellow crystals were obtained after 2 months. The crystals are of poor quality, fragile and usually twinned. The ligand (2-pyridinecarboxaldehyde benzoylhydrazone) was prepared according to Khalil *et al.* (1994) and recrystallized a minimum of three times from hot methanol.

Crystal data

$[Ce(NO_3)_3(C_{13}H_{11}N_3O)_2]\cdot C_3H_6O\cdot 2H_2O$
$M_r = 870.76$
Monoclinic
$P2_1/n$
$a = 18.6342\,(19)$ Å
$b = 11.1941\,(8)$ Å
$c = 34.734\,(2)$ Å
$\beta = 99.188\,(9)°$
$V = 7152.3\,(10)$ Å^3
$Z = 8$
$D_x = 1.617$ Mg m^{-3}
$D_m = 1.59$ Mg m^{-3}
D_m measured by flotation in $CCl_4/CHCl_3$

Mo $K\alpha$ radiation
$\lambda = 0.71070$ Å
Cell parameters from 24 reflections
$\theta = 15.05–18.15°$
$\mu = 1.352$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.60 × 0.36 × 0.27 mm
Yellow

Data collection

Upgraded Philips PW1100 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*EMPIR*; Stoe & Cie, 1988*b*)
$T_{\min} = 0.545$, $T_{\max} = 0.694$
13 582 measured reflections
12 484 independent reflections

7456 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\max} = 25.01°$
$h = -22 \rightarrow 21$
$k = -5 \rightarrow 13$
$l = -16 \rightarrow 41$
3 standard reflections
frequency: 120 min
intensity decay: 14%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.116$
$S = 0.945$
12 484 reflections
959 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0674P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.048$
$\Delta\rho_{\max} = 1.127$ e Å^{-3}
$\Delta\rho_{\min} = -0.935$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ce1—O2*A*	2.528 (3)	Ce2—O1*B*	2.530 (3)
Ce1—O1*A*	2.585 (3)	Ce2—O2*B*	2.583 (4)
Ce1—O9*A*	2.607 (4)	Ce2—O10*B*	2.601 (4)
Ce1—O3*A*	2.634 (4)	Ce2—O9*B*	2.650 (4)
Ce1—O10*A*	2.657 (4)	Ce2—O3*B*	2.661 (4)
Ce1—O6*A*	2.674 (4)	Ce2—O7*B*	2.673 (4)
Ce1—N2*A*	2.725 (4)	Ce2—O4*B*	2.717 (4)
Ce1—O7*A*	2.724 (4)	Ce2—N2*B*	2.731 (4)
Ce1—N5*A*	2.744 (4)	Ce2—O6*B*	2.740 (4)
Ce1—O4*A*	2.759 (4)	Ce2—N5*B*	2.750 (4)
Ce1—N3*A*	2.800 (4)	Ce2—N6*B*	2.790 (4)
Ce1—N6*A*	2.848 (4)	Ce2—N3*B*	2.838 (4)
O9*A*—Ce1—O10*A*	48.35 (12)	O10*B*—Ce2—O9*B*	48.43 (13)
O1*A*—Ce1—N2*A*	58.01 (11)	O3*B*—Ce2—O4*B*	46.95 (11)
O6*A*—Ce1—O7*A*	46.82 (11)	O1*B*—Ce2—N2*B*	58.81 (12)
O2*A*—Ce1—N5*A*	58.43 (11)	O7*B*—Ce2—O6*B*	46.60 (11)
O3*A*—Ce1—O4*A*	46.66 (11)	O2*B*—Ce2—N5*B*	57.57 (11)
N2*A*—Ce1—N3*A*	58.50 (12)	N5*B*—Ce2—N6*B*	58.46 (12)
N5*A*—Ce1—N6*A*	57.52 (12)	N2*B*—Ce2—N3*B*	57.55 (13)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*A*—H1*A*···O4*W*	0.86	1.96	2.815 (6)	171.9
N4*A*—H4*A*1···O2*W*	0.86	2.04	2.883 (6)	164.8
N1*B*—H1*B*···O1*W*	0.86	1.99	2.830 (6)	164.5
N4*B*—H4*B*1···O3*W*	0.86	2.03	2.872 (6)	167.6

All non-H atoms were refined with anisotropic displacement parameters. The H atoms, except those of the water molecules, were placed at their calculated positions and were constrained to ride on the atoms to which they were bonded (aromatic C—H = 0.93, Csp^3 = 0.96 and N—H = 0.86 Å), with displacement parameters set at $1.2U_{\rm eq}$ of those atoms.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*c*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *DIAMOND* (Bergerhoff, 1996). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1012). Services for accessing these data are described at the back of the journal.

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Polymeric aqua-1κO-bis[μ-(R,R)-tartrato-1κ^2O^1,O^2:2κ^2O^3,O^4]dicadmium(II) trihydrate

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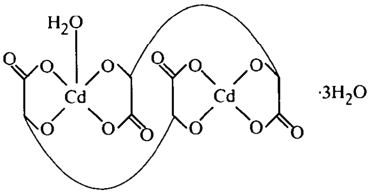
(*Received 9 September 1998; accepted 11 January 1999*)

Abstract

The structure of the title compound, {[$Cd_2(C_4H_4O_6)_2(H_2O)$]·$3H_2O$}$_n$, consists of corrugated polymeric sheets of dimeric [$Cd_2(C_4H_4O_6)_2(H_2O)$] units and three water molecules of crystallization. Both cadmium ions are coordinated by two (R,R)-tartrate ligands in a *cis* arrangement, and the octahedral geometry for each cation is completed by two carboxyl O atoms of different neighbouring dimers or by one carboxyl O atom and a water molecule. Additional water molecules are held in the crystal lattice, forming a hydrogen-bonding network to keep the dimers together in the non-planar sheets.

Comment

This work is part of a research project concerning the investigation of the dielectric properties of tartrate salts with divalent cations as related to their crystalline structure. The electrical properties of cadmium tartrate, as well as the X-ray diffraction powder patterns, reveal the occurrence of two successive phase changes of structural origin (Torres *et al.*, 1998). In order to investigate the transition mechanisms, the structure of a single crystal of the title compound, (I), at room temperature, has been solved.



(I)

The smallest structural subunit appears to be the dimeric entity [$Cd_2(C_4H_4O_6)_2(H_2O)$] (Fig. 1). The bond geometry for each tartrate is usual and does not deviate significantly from that of the reported pseudo-isomorphous tartrate complexes of Ni, Cu, Zn and Mn (Bostelaar *et al.*, 1984; Prout *et al.*, 1971; Templeton *et al.*, 1985; Ruiz-Pérez *et al.*, 1996). Bond lengths averaged for the two tartrates are C—C 1.529 (5), C—O(hydroxyl) 1.419 (4) and C—O(carboxyl) 1.254 (5) Å, and the averaged bond angles are C—C—C 110.8 (3), C—C—O(hydroxyl) 110.6 (3), C—C—O(carboxyl) 117.5 (3) and O—C═O 124.8°. Each Cd^{2+} ion is coordinated by two halves of two different tartrate dianions *via* chelation through the hydroxyl and the carboxyl groups. Such chelate rings (–Cd—OCCO–) are nearly planar; the mean deviation from the least-squares plane varies between 0.0203 and 0.0665 Å. The octahedral coordination geometry around the Cd1 atom is completed by a water molecule (O*W*1) and a non-chelating carboxylate O atom (O8*a*) of another dimer. The sixfold coordination of the Cd2 atom is com-

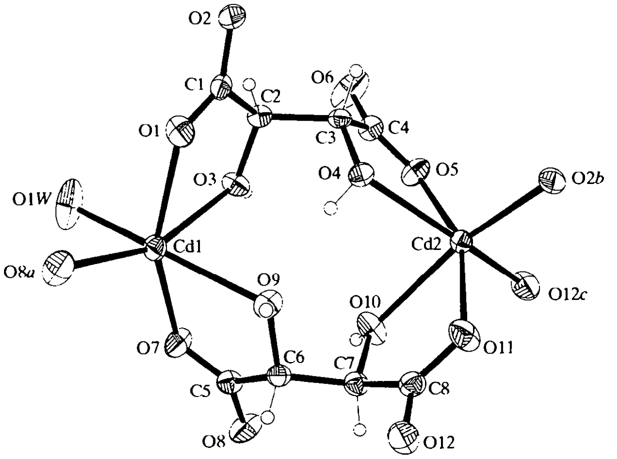


Fig. 1. Perspective drawing of the dimeric unit of the title compound showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. Water molecules O2*W*, O3*W* and O4*W* have been omitted for clarity. Symmetry codes: (*a*) $\frac{1}{2}+x, -\frac{3}{2}-y, -1-z$; (*b*) $-x, \frac{1}{2}+y, -\frac{1}{2}-z$; (*c*) $x-\frac{1}{2}, -\frac{1}{2}-y, -1-z$.