

Acta Cryst. (1996). **C52**, 1449–1451**Cerium 3,5-Dinitrobenzoate Dihydrate**M. NAWAZ TAHIR,^{a*} DİNÇER ÜLKÜ,^a CANAN ÜNALEROĞLU^b AND ELMAN M. MÖVSÜMOV^b^a*Department of Physics Engineering, Hacettepe University, Beytepe 06532, Ankara, Turkey, and* ^b*Department of Chemistry, Hacettepe University, Beytepe 06532, Ankara, Turkey. E-mail: ftahir@eti.cc.hun.edu.tr*

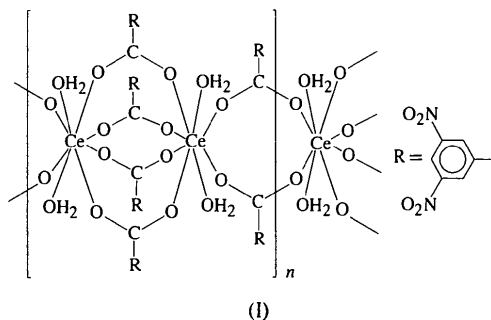
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Abstract

In the crystal structure of the title molecule, *catenapoly*[[tetraaqua-1 κ^2 O, 2 κ^2 O-tetrakis(μ -3,5-dinitrobenzoato-O:O')dicerium]-bis(μ -3,5-dinitrobenzoato-O:O')], [Ce₂(C₇H₃N₂O₆)₆(H₂O)₄], cerium ions are bridged by carboxylate groups to form linear polymeric chains. The coordination around Ce is eightfold involving six O atoms from six carboxylate groups and two water O atoms. Within the polymeric chains, only the bridging type of bonding exists. Ce—O distances vary between 2.400 (5) and 2.661 (5) Å, resulting in a strongly distorted square-antiprism arrangement around Ce.

Comment

Structural studies of rare earth carboxylates have shown that the carboxylate groups may be coordinated simultaneously in three modes, namely, chelating, bridging and chelating-bridging (Ma, Jin & Ni, 1994*a,b*; Hiyalov, Amirasanov, Mamedov & Mövsümov, 1981; Bats, Klaus & Fuess, 1979; Moore, Glick & Baker, 1971). In the present study, we describe the structure of the title compound, (I), which shows only the bridging type of bonding within the polymeric chain. The reason for the single-mode coordination might be the simultaneous occurrence of two nitro groups. As can be seen from the chemical diagram, Ce ions are bridged alternately by four and two ligands, resulting in two different Ce...Ce distances of 4.2824 (7) and 5.3786 (8) Å, respectively.



Each Ce ion is coordinated to six carboxylate O atoms (O1, O2, O3, O4, O5, O6) and two water O atoms (O7, O8) (Fig. 1). The nitro groups are not coordinated to the Ce ion. The Ce—O distances of the bridging carboxylate groups [2.400 (5)–2.507 (5) Å] are shorter than the Ce—O distances [2.603 (6)–2.661 (5) Å] involving the water molecules. A comparison of (I) with known related compounds shows that the average Ce—O distance found here (2.499 Å) is slightly shorter than the value reported for ceric ammonium nitrate [2.508 (7) Å; Beineke & Delgaudio, 1968], but larger than that found in both [Ce(IO₃)₄] [2.31 (9) Å; Cromer & Allen, 1956] and cerium acetylacetonate [2.395 Å; Matković & Gredenić, 1963].

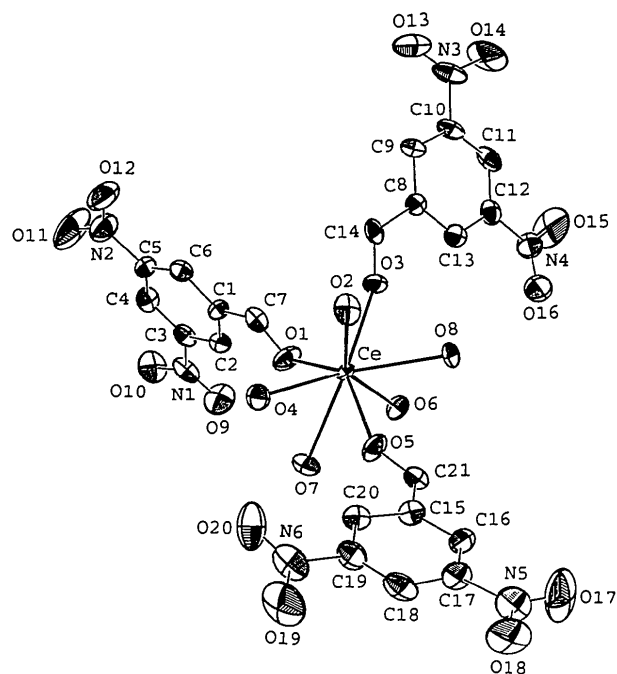


Fig. 1. An ORTEP (Johnson, 1965) drawing of the asymmetric unit of the title compound with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

The average C—C distance in the aromatic ring of the 3,5-dinitrobenzoate ligand is 1.38 (1) Å and the average C—N, C—O and N—O distances are 1.48 (1), 1.25 (1) and 1.214 (6) Å, respectively. Details of the hydrogen-bonding geometry involving the water molecules are given in Table 3.

Experimental

An aqueous solution of sodium 3,5-dinitrobenzoate was added to an aqueous solution of CeCl₃·6H₂O (1:1 molar ratio) and single crystals were obtained by slow evaporation of the final solution.

Crystal data

[Ce₂(C₇H₃N₂O₆)₆(H₂O)₄]
M_r = 1618.97
 Triclinic
*P*1̄
a = 9.531 (1) Å
b = 12.120 (1) Å
c = 14.327 (2) Å
 α = 64.34 (2)°
 β = 70.61 (1)°
 γ = 82.90 (1)°
V = 1406.9 (7) Å³
Z = 1
D_x = 1.91 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 8.44–20.08°
 μ = 1.73 mm⁻¹
T = 295 K
 Needle
 0.25 × 0.125 × 0.1 mm
 Colourless

N3	1.4096 (8)	0.1288 (6)	-0.5974 (5)	3.5 (2)
N4	0.8710 (8)	0.1601 (6)	-0.5181 (5)	3.5 (2)
N5	0.1304 (9)	-0.5361 (6)	0.4120 (6)	4.7 (2)
N6	0.4332 (8)	-0.3846 (6)	0.5501 (5)	3.8 (2)
C1	1.0604 (8)	0.3691 (6)	-0.0985 (5)	1.8 (2)
C2	0.9726 (8)	0.4742 (6)	-0.1223 (5)	2.1 (2)
C3	1.0332 (9)	0.5824 (6)	-0.1441 (5)	2.4 (2)
C4	1.1735 (9)	0.5945 (7)	-0.1439 (5)	2.8 (2)
C5	1.2579 (8)	0.4911 (7)	-0.1211 (5)	2.6 (2)
C6	1.2041 (8)	0.3777 (6)	-0.0997 (5)	2.3 (2)
C7	0.9931 (9)	0.2455 (6)	-0.0662 (5)	2.3 (2)
C8	1.1058 (8)	0.0770 (6)	-0.3369 (5)	1.9 (2)
C9	1.2499 (9)	0.0856 (6)	-0.4105 (5)	2.3 (2)
C10	1.2601 (9)	0.1202 (7)	-0.5173 (5)	2.6 (2)
C11	1.1417 (9)	0.1447 (7)	-0.5564 (5)	2.8 (2)
C12	1.0023 (9)	0.1320 (6)	-0.4799 (5)	2.5 (2)
C13	0.9835 (9)	0.1004 (6)	-0.3727 (5)	2.4 (2)
C14	1.0834 (8)	0.0450 (6)	-0.2185 (5)	2.2 (2)
C15	0.3933 (8)	-0.2695 (6)	0.2741 (5)	2.3 (2)
C16	0.2879 (8)	-0.3524 (7)	0.2926 (6)	2.6 (2)
C17	0.2352 (9)	-0.4432 (7)	0.3944 (6)	3.0 (2)
C18	0.275 (1)	-0.4542 (7)	0.4823 (6)	3.4 (2)
C19	0.3817 (9)	-0.3725 (7)	0.4602 (6)	2.9 (2)
C20	0.4448 (9)	-0.2822 (6)	0.3585 (5)	2.4 (2)
C21	0.4547 (8)	-0.1676 (6)	0.1640 (5)	2.1 (2)

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scans (MolEN; Fair, 1990)
T_{min} = 0.788, *T_{max}* = 0.999
 5798 measured reflections
 5118 independent reflections

3492 observed reflections
 $[I > 3\sigma(I)]$
R_{int} = 0.030
 θ_{\max} = 26.32°
h = 0 → 11
k = -14 → 15
l = -16 → 17
 3 standard reflections
 frequency: 120 min
 intensity decay: 0.85%

Refinement

Refinement on *F*²
R = 0.044
wR = 0.044
S = 1.08
 3264 reflections
 433 parameters
 $w = 1/\sigma^2(F)$
 $(\Delta/\sigma)_{\max} = 0.00031$

$\Delta\rho_{\max} = 1.365 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.803 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 2. Selected geometric parameters (Å, °)

Ce—O1	2.507 (5)	Ce—O5	2.419 (4)
Ce—O2	2.448 (5)	Ce—O6	2.400 (5)
Ce—O3	2.415 (4)	Ce—O7	2.661 (5)
Ce—O4	2.473 (6)	Ce—O8	2.603 (6)
O1—Ce—O2	124.9 (2)	O3—Ce—O7	138.9 (1)
O1—Ce—O3	77.6 (2)	O3—Ce—O8	68.9 (2)
O1—Ce—O4	86.3 (2)	O4—Ce—O5	75.7 (2)
O1—Ce—O5	139.2 (2)	O4—Ce—O6	136.6 (2)
O1—Ce—O6	76.8 (2)	O4—Ce—O7	70.3 (2)
O1—Ce—O7	67.4 (2)	O4—Ce—O8	138.4 (2)
O1—Ce—O8	135.0 (2)	O5—Ce—O6	91.5 (2)
O2—Ce—O3	74.8 (2)	O5—Ce—O7	72.1 (2)
O2—Ce—O4	76.4 (2)	O5—Ce—O8	73.5 (2)
O2—Ce—O5	86.4 (2)	O6—Ce—O7	66.3 (2)
O2—Ce—O6	145.1 (2)	O6—Ce—O8	71.7 (2)
O2—Ce—O7	143.7 (2)	O7—Ce—O8	123.8 (2)
O2—Ce—O8	74.4 (2)	Ce—O1—C7	111.2 (4)
O3—Ce—O4	129.5 (2)	Ce—O3—C14	150.4 (5)
O3—Ce—O5	141.2 (2)	Ce—O5—C21	144.5 (5)
O3—Ce—O6	85.7 (2)		

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
Ce	0.77017 (5)	0.02652 (4)	0.00962 (3)	1.362 (8)
O1	0.8595 (6)	0.2421 (5)	-0.0592 (4)	3.3 (1)
O2	0.9265 (6)	-0.1538 (4)	0.0473 (4)	3.0 (1)
O3	0.9538 (5)	0.0582 (5)	-0.1637 (3)	2.6 (1)
O4	0.8055 (6)	-0.0079 (5)	0.1835 (4)	2.9 (1)
O5	0.5659 (6)	-0.1100 (5)	0.1480 (4)	3.0 (1)
O6	0.6102 (5)	0.1458 (4)	-0.0951 (3)	2.3 (1)
O7	0.5747 (6)	0.1554 (4)	0.1017 (4)	3.0 (1)
O8	0.7028 (6)	-0.1008 (4)	-0.0771 (4)	3.0 (1)
O9	0.8125 (7)	0.6791 (5)	-0.1663 (5)	4.7 (2)
O10	0.9846 (7)	0.7838 (5)	-0.1695 (5)	4.5 (2)
O11	1.4459 (8)	0.5947 (6)	-0.1248 (6)	8.1 (2)
O12	1.4819 (7)	0.4075 (6)	-0.1008 (5)	5.4 (2)
O13	1.5196 (7)	0.1237 (6)	-0.5710 (5)	5.0 (2)
O14	1.4137 (9)	0.1387 (7)	-0.6874 (4)	7.3 (2)
O15	0.8895 (8)	0.2123 (8)	-0.6144 (5)	7.1 (2)
O16	0.7522 (7)	0.1227 (6)	-0.4480 (4)	4.6 (2)
O17	0.0933 (9)	-0.5259 (7)	0.3363 (5)	8.8 (2)
O18	0.0860 (8)	-0.6173 (5)	0.5033 (5)	5.6 (2)
O19	0.3639 (9)	-0.4554 (7)	0.6422 (5)	6.4 (2)
O20	0.5454 (7)	-0.3294 (6)	0.5281 (4)	5.1 (2)
N1	0.9357 (8)	0.6902 (5)	-0.1621 (4)	3.1 (2)
N2	1.4076 (8)	0.4990 (6)	-0.1157 (6)	4.2 (2)

Table 3. 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>
O7—H71...O12 ⁱ	0.96	2.59	3.449 (8)	150
O7—H72...O14 ⁱⁱ	0.92	1.92	2.827 (8)	168
O8—H81...O10 ⁱⁱⁱ	0.94	2.26	3.039 (8)	140
O8—H82...O7 ^{iv}	1.02	2.11	2.968 (9)	140

Symmetry codes: (i) *x* - 1, *y*, *z*; (ii) *x* - 1, *y*, 1 + *z*; (iii) *x*, *y* - 1, *z*; (iv) 1 - *x*, -*y*, -*z*.

H atoms bonded to C atoms were placed geometrically 1.05 Å from their bonded atoms, while the water H atoms were taken from a difference map. All H-atom displacement parameters were fixed as 1.3 times those of their bonded atoms. A riding model was used for all H atoms.

Data collection: *CAD-4 EXPRESS Software* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN SIMPEL*. Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *MolEN ORTEP* (Johnson, 1965). Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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