

Hexaamminecobalt(III) aqua-bis(nitrilotriacetato- $\kappa^4 N, O, O', O''$)-gadolinate(III) octahydrate

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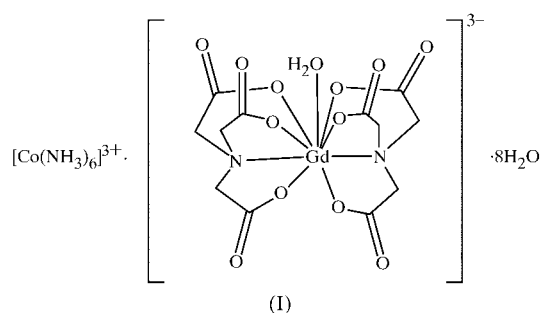
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Crystals of the title compound, $[\text{Co}(\text{NH}_3)_6][\text{Gd}(\text{C}_6\text{H}_6\text{NO}_6)_2 \cdot (\text{H}_2\text{O})] \cdot 8\text{H}_2\text{O}$, were synthesized in and collected from aqueous solution. The hexaamminecobalt(III) cation has the expected octahedral geometry, while the Gd coordination sphere has the geometry of a tricapped trigonal prism, with the two nitrilotriacetate N atoms and one water molecule occupying the capping positions.

Comment

Gadolinium complexes have found widespread use as contrast agents in magnetic resonance imaging (MRI), with an estimate of over 30 tonnes of Gd having been administered since the first commercial Gd contrast agent was approved by the US Food and Drug Administration (FDA) for use in humans in 1988 (Caravan *et al.*, 1999; Lauffer, 1987). Each of these compounds is composed of an octadentate chelating ligand and one coordinating water molecule, forming a nine-coordinate complex. A search of Version 5.22 of the Cambridge Structural Database (Allen & Kennard, 1993) identified only 298 structures of Gd complexes. Our synthesis of Gd–nitrilotriacetate (Gd–NTA) complexes is part of an effort to increase this number, and the structure of the title Gd–NTA complex, (I), is presented here.



A bis(NTA)gadolinate complex with a $[\text{Gd}(\text{H}_2\text{O})_x]^{3+}$ counter-ion was synthesized by Parrish *et al.* (1998) from a 1:1 mixture of gadolinium chloride and NTA. The compound was found to have a high degree of disorder, in particular in the

aqua–Gd cation, as well as either an inconveniently long cell length, $c = 80.83(2)$ Å, or a twinning problem.

The synthesis of (I) was undertaken in order to try to eliminate some of the problems in the original structure. Hexaamminecobalt(III) chloride was used to precipitate the anionic complex, thus eliminating the largest single source of disorder. Orange crystals of (I) formed from an aqueous 2:1 mole ratio mixture of NTA with hexaamminecobalt(III) chloride and an excess of gadolinium(III) chloride (the hygroscopic nature of the starting material precludes exact molar quantification).

Complex (I) (Fig. 1) is nine-coordinate, as are 43% of the previously reported complexes (Allen & Kennard, 1993) and 100% of FDA-approved MRI contrast agents (Caravan *et al.*, 1999). The complex is a tricapped trigonal prism (Fig. 2), as is common for nine-coordinate complexes (Guggenberger & Muetterties, 1976). Bond distances and angles for the coordination sphere of (I) are given in Table 1. The O atom of the coordinated water molecule and the two NTA N atoms occupy the capping positions. Of the eight non-coordinated water molecules, six form one hydrogen bond with carboxylate groups, while the remaining two each form hydrogen bonds

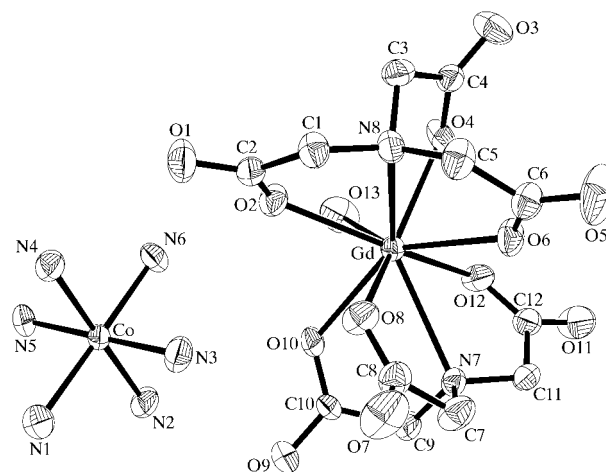


Figure 1

A view of the structure of (I), showing the discrete anion and cation pair. Displacement ellipsoids are drawn at the 50% probability level, and H atoms and water molecules of hydration have been omitted for clarity.

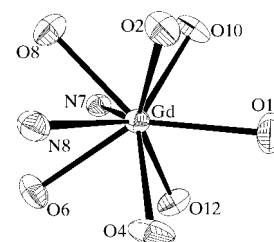


Figure 2

The coordination sphere of the gadolinate anion, showing the tricapped trigonal prism geometry with atoms N7, N8 and O13 occupying the capping positions. Displacement ellipsoids are drawn at the 50% probability level.

with two separate carboxylate groups. The locations of the H atoms of the water molecules were not observed experimentally and were not included. There appeared to be some disorder in the water molecules of hydration, but it was not possible to separate individual positions within the electron density.

The Co coordination sphere in (I) is octahedral, with Co—N distances in the range 1.962 (6)–1.981 (7) Å, and N—Co—N angles in the range 88.5 (3)–91.5 (3)° for *cis* N atoms and 178.8 (3)–179.4 (3)° for *trans* N atoms.

Experimental

Hexaamminecobalt(III) chloride (0.1652 g, 0.6176 mmol), the disodium salt of nitrilotriacetic acid (0.2816 g, 1.198 mmol) and gadolinium(III) chloride (approximately 1 mmol) were dissolved in water (approximately 50 ml); gadolinium chloride is hygroscopic, so an excess was used to ensure that nitrilotriacetic acid was the limiting reagent. The solvent was allowed to evaporate slowly over the course of a week, resulting in the formation of orange plates. A 26.1% yield (0.1338 g) of (I) was recovered from the reaction mixture. Elemental analyses were in agreement with the crystallographic data (expected for C₁₂H₄₈CoGdN₈O₂₁: C 16.82, H 5.65, N 13.08%; found: C 16.80, H 5.92, N 13.07%). Attempts to determine the melting point of the product failed, as the compound was found to decompose with a visible loss of liquid, presumably water, at approximately 373 K, leaving a red solid residue. This solid was found to have low solubility in water, but was not further characterized.

Crystal data

[Co(NH₃)₆][Gd(C₆H₆NO₆)₂·(H₂O)]·8H₂O
M_r = 856.76
 Monoclinic, *P*2₁/*n*
a = 11.760 (2) Å
b = 20.625 (4) Å
c = 14.109 (3) Å
 β = 113.55 (3)°
V = 3137.1 (13) Å³
Z = 4
D_x = 1.814 Mg m⁻³

D_m = 1.77 (3) Mg m⁻³
D_m measured by flotation in 1,2-dibromoethane and pentane
 Mo *K*α radiation
 Cell parameters from 28 reflections
 θ = 1.5–27.5°
 μ = 2.72 mm⁻¹
T = 293 (2) K
 Plate, light orange
 0.40 × 0.29 × 0.20 mm

Data collection

Bruker R3 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: ψ scan (SHELXTL-Plus; Sheldrick, 1990)
T_{min} = 0.361, *T_{max}* = 0.581
 7452 measured reflections
 7126 independent reflections
 5526 reflections with *I* > 2σ(*I*)

R_{int} = 0.056
 θ_{\max} = 27.6°
h = 0 → 15
k = 0 → 26
l = -18 → 16
 3 standard reflections every 50 reflections
 intensity decay: 16%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.058
wR(*F*²) = 0.172
S = 1.12
 7126 reflections
 394 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0968P)^2 + 15.8892P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.028$
 $\Delta\rho_{\max} = 3.76 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -4.27 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Gd—O4	2.342 (6)	Gd—O12	2.412 (5)
Gd—O10	2.399 (5)	Gd—O13	2.449 (6)
Gd—O6	2.399 (5)	Gd—N8	2.674 (6)
Gd—O8	2.403 (5)	Gd—N7	2.682 (6)
Gd—O2	2.411 (5)		
O4—Gd—O10	146.3 (2)	O8—Gd—O13	139.3 (2)
O4—Gd—O6	73.3 (2)	O2—Gd—O13	75.4 (2)
O10—Gd—O6	137.14 (19)	O12—Gd—O13	76.1 (2)
O4—Gd—O8	136.9 (2)	O4—Gd—N8	66.90 (18)
O10—Gd—O8	73.4 (2)	O10—Gd—N8	131.94 (18)
O6—Gd—O8	79.8 (2)	O6—Gd—N8	65.22 (18)
O4—Gd—O2	95.01 (18)	O8—Gd—N8	71.54 (19)
O10—Gd—O2	76.83 (18)	O2—Gd—N8	63.51 (17)
O6—Gd—O2	127.81 (18)	O12—Gd—N8	133.31 (19)
O8—Gd—O2	75.77 (18)	O13—Gd—N8	118.4 (2)
O4—Gd—O12	77.25 (17)	O4—Gd—N7	131.73 (18)
O10—Gd—O12	94.34 (19)	O10—Gd—N7	67.33 (17)
O6—Gd—O12	76.74 (19)	O6—Gd—N7	71.33 (18)
O8—Gd—O12	128.19 (17)	O8—Gd—N7	65.37 (17)
O2—Gd—O12	151.47 (19)	O2—Gd—N7	132.74 (18)
O4—Gd—O13	73.7 (2)	O12—Gd—N7	63.53 (17)
O10—Gd—O13	72.6 (2)	O13—Gd—N7	118.97 (19)
O6—Gd—O13	140.9 (2)	N8—Gd—N7	122.66 (19)

The H atoms of the water molecules were not located. H atoms on C and N atoms were treated as riding, with N—H distances of 0.89 Å and C—H distances of 0.97 Å. The highest peak in the difference map is 0.76 Å and the deepest hole 0.63 Å from the Gd atom.

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1390). Services for accessing these data are described at the back of the journal.

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