Crystal structure of dinitratobis(4-methyl-5-formyl-imidazolfuranoylhydrazone)gadolinium(III) mononitrate, $[\text{Gd}\{(\text{OC}(\text{C}_4\text{H}_3\text{O})\text{NHNCH}(\text{CH}_3)\text{C}_3\text{H}_2\text{N}_2)\}_2(\text{NO}_3)_2][\text{NO}_3]$

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Abstract

$\text{C}_{20}\text{H}_{20}\text{GdN}_{11}\text{O}_{13}$, triclinic, $P\bar{1}$ (no. 2), $a = 8.1732(1)$ Å, $b = 10.8640(2)$ Å, $c = 16.2532(3)$ Å, $\alpha = 109.0304(8)^\circ$, $\beta = 94.6800(7)^\circ$, $\gamma = 96.127(1)^\circ$, $V = 1346.1$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.048$, $wR_{\text{ref}}(F^2) = 0.132$, $T = 173$ K.

Source of material

4-methyl-5-formylimidazole (10 mmol) and furanoic hydrazide (10 mmol) were dissolved in ethanol with gentle warming. The white product which separated after the concentration of the solution was filtered, washed with ice cold ethanol and diethyl ether and dried in vacuo to obtain 4-methyl-5-formyl-imidazolfuranoylhydrazone (H_2L). An ethanol solution of $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2 mmol) was then added to an ethanolic solution of the ligand (4 mmol). After heating and stirring for two hours the gadolinium complex was obtained as a yellow precipitate after evaporation of the solvent. Crystals of $[\text{Gd}(\text{H}_2\text{L})_2(\text{NO}_3)_2]\text{NO}_3$ were grown by slow evaporation from an ethanol solution.

Discussion

The gadolinium(III) ion is linked to four nitrogen atoms and two oxygen atoms from the molecules of ligand, and four oxygen atoms from the nitrate ions acting as bidentate. The coordination of the hydrazones to Gd results in the formation of two five-mem-

bered chelating rings per ligand molecule. In the rings the Gd—N bonds are the largest metal-ligand distances ($d(\text{Gd—N1}) = 2.578(4)$ Å, $d(\text{Gd—N2}) = 2.587(4)$ Å, $d(\text{Gd—N3}) = 2.639(4)$ Å, $d(\text{Gd—N5}) = 2.665(4)$ Å). The Gd—O bonds, involving the hydrazonic oxygen, are the shortest metal-ligand distances and are comparable in the two ligand molecules ($d(\text{Gd—O1}) = 2.487(3)$ Å and $d(\text{Gd—O8}) = 2.488(3)$ Å). The following bonds are not altered in the complex: C14—N3 and C8—N5 are consistent with a double bond and C6—N6 and C29—N4 are consistent with a single bond. The remaining bond distances of the hydrazone moiety as well as C4—O1 and C16—O8 are slightly different in the two ligand molecules being 1.249(5) Å and 1.242(6) Å, respectively. Two of the three nitrate moieties act as bidentate while the last one remains uncoordinated. The bond angles of the two ligand molecules, which involve the Gd(III) ion are very similar ($\angle\text{O1—Gd—N5} = 59.7(1)^\circ$, $\angle\text{N1—Gd—N5} = 61.6(1)^\circ$, $\angle\text{O8—Gd—N3} = 60.0(1)^\circ$ and $\angle\text{N2—Gd—N3} = 61.6(1)^\circ$). The gadolinium atom is ten-coordinated. Its coordination polyhedron can be described as a bi-capped square antiprism [1].

Table 1. Data collection and handling.

Crystal:	yellow, prismatic, size $0.1 \times 0.1 \times 0.1$ mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ :	25.52 cm^{-1}
Diffractionmeter, scan mode:	Nonius KappaCCD, ω/ϕ
$2\theta_{\text{max}}$:	60.08°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	17609, 7840
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 6224
$N(\text{param})_{\text{refined}}$:	406
Programs:	SHELXS-86 [2], SHELXL-97 [3], ORTEP-II [4], WinGX [5], PLATON [6]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1)	2i	0.3846	0.1354	0.1685	0.033
H(2)	2i	1.1839	0.7938	0.3370	0.029
H(3)	2i	1.0676	0.2712	−0.0517	0.061
H(4)	2i	0.6928	0.4520	0.6025	0.046
H(5)	2i	0.8610	0.5581	0.5206	0.030
H(6)	2i	0.4996	0.2177	0.5576	0.040
H(7)	2i	0.4167	0.1607	0.4576	0.040
H(8)	2i	0.3560	0.2862	0.5248	0.040
H(9)	2i	1.2300	0.6629	0.1954	0.032
H(10)	2i	0.4288	0.1708	0.3192	0.031

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Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(11)	2i	1.3013	0.4585	-0.0369	0.046
H(12)	2i	1.3958	0.4781	0.0577	0.046
H(13)	2i	1.2995	0.5915	0.0431	0.046
H(14)	2i	0.1649	-0.0294	-0.1276	0.073
H(15)	2i	0.3631	0.1096	-0.1732	0.080

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(16)	2i	1.0989	1.0054	0.6837	0.057
H(17)	2i	0.9023	0.8241	0.5685	0.042
H(18)	2i	0.5440	0.2655	-0.0433	0.033
H(19)	2i	0.8450	0.2256	0.0305	0.039
H(20)	2i	1.3377	1.0600	0.6161	0.052

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Gd(1)	2i	0.79313(3)	0.45533(2)	0.26408(1)	0.0194(1)	0.0234(1)	0.0199(1)	-0.00010(9)	0.00301(8)	0.00759(9)
O(1)	2i	0.8907(4)	0.6550(3)	0.3944(2)	0.024(2)	0.022(2)	0.024(2)	-0.003(1)	0.006(1)	0.005(1)
O(2)	2i	0.7141(5)	0.6349(4)	0.2127(3)	0.038(2)	0.039(2)	0.037(2)	0.008(2)	0.010(2)	0.022(2)
O(3)	2i	0.5090(5)	0.7431(4)	0.2583(3)	0.035(2)	0.035(2)	0.079(3)	0.012(2)	-0.002(2)	0.017(2)
O(4)	2i	0.5451(4)	0.5688(4)	0.2903(2)	0.029(2)	0.038(2)	0.037(2)	0.004(2)	0.010(2)	0.014(2)
O(5)	2i	1.0589(4)	0.3952(3)	0.3105(2)	0.029(2)	0.027(2)	0.031(2)	0.000(1)	-0.003(2)	0.007(2)
O(6)	2i	1.1195(5)	0.1959(4)	0.2700(3)	0.037(2)	0.040(2)	0.077(3)	0.021(2)	0.011(2)	0.025(2)
O(7)	2i	0.8700(4)	0.2336(3)	0.2395(2)	0.026(2)	0.028(2)	0.034(2)	-0.002(1)	0.000(2)	0.006(2)
O(8)	2i	0.6059(4)	0.3440(3)	0.1248(2)	0.024(2)	0.032(2)	0.023(2)	-0.003(1)	0.002(1)	0.011(1)
O(9)	2i	1.2238(5)	0.9183(4)	0.4988(3)	0.041(2)	0.039(2)	0.038(2)	-0.011(2)	0.003(2)	0.004(2)
O(10)	2i	0.2813(7)	0.0739(5)	0.0050(3)	0.068(3)	0.058(3)	0.066(3)	-0.010(3)	-0.015(3)	0.013(3)
O(11)	2i	0.2783(5)	0.9545(4)	0.3006(3)	0.037(2)	0.036(2)	0.056(3)	-0.003(2)	-0.004(2)	0.012(2)
O(12)	2i	0.0675(6)	0.8693(4)	0.2001(3)	0.058(3)	0.043(2)	0.036(2)	-0.011(2)	0.000(2)	0.013(2)
O(13)	2i	0.2880(8)	0.9661(5)	0.1694(4)	0.112(5)	0.040(3)	0.076(4)	0.005(3)	0.066(3)	0.022(3)
N(1)	2i	0.9468(5)	0.4014(4)	0.1270(3)	0.026(2)	0.027(2)	0.023(2)	0.004(2)	0.004(2)	0.004(2)
N(2)	2i	0.7259(5)	0.4225(4)	0.4089(3)	0.022(2)	0.027(2)	0.022(2)	-0.003(2)	0.001(2)	0.009(2)
N(3)	2i	0.5410(5)	0.2780(4)	0.2577(3)	0.019(2)	0.030(2)	0.021(2)	-0.001(2)	0.002(2)	0.009(2)
N(4)	2i	0.4585(5)	0.2048(4)	0.1769(3)	0.027(2)	0.029(2)	0.022(2)	-0.008(2)	-0.001(2)	0.007(2)
N(5)	2i	1.0539(5)	0.6240(4)	0.2625(3)	0.023(2)	0.024(2)	0.022(2)	0.000(2)	0.004(2)	0.006(2)
N(6)	2i	1.1023(5)	0.7323(4)	0.3345(3)	0.024(2)	0.023(2)	0.022(2)	-0.005(2)	0.005(2)	0.004(2)
N(7)	2i	1.0527(7)	0.3220(6)	0.0009(3)	0.056(3)	0.060(4)	0.040(3)	0.026(3)	0.013(3)	0.015(3)
N(8)	2i	0.6840(6)	0.4284(5)	0.5449(3)	0.044(3)	0.042(3)	0.033(2)	0.007(2)	0.010(2)	0.016(2)
N(9)	2i	1.0198(5)	0.2725(4)	0.2738(3)	0.031(2)	0.028(2)	0.029(2)	0.007(2)	0.009(2)	0.013(2)
N(10)	2i	0.5863(5)	0.6508(4)	0.2532(3)	0.021(2)	0.021(2)	0.049(3)	-0.000(2)	-0.011(2)	0.008(2)
N(11)	2i	0.2094(7)	0.9300(4)	0.2224(3)	0.054(3)	0.023(2)	0.044(3)	0.003(2)	0.025(2)	0.010(2)
C(1)	2i	0.7754(6)	0.4854(5)	0.4967(3)	0.024(2)	0.025(2)	0.028(2)	-0.003(2)	0.000(2)	0.011(2)
C(2)	2i	0.5760(5)	0.3271(4)	0.4858(3)	0.015(2)	0.017(2)	0.012(2)	-0.002(2)	0.003(1)	0.005(2)
C(3)	2i	0.4519(6)	0.2409(5)	0.5083(4)	0.031(3)	0.035(3)	0.032(3)	-0.004(2)	0.009(2)	0.013(2)
C(4)	2i	1.0141(6)	0.7375(5)	0.4019(3)	0.025(2)	0.021(2)	0.023(2)	0.004(2)	0.005(2)	0.010(2)
C(5)	2i	1.1374(6)	0.6031(5)	0.1968(3)	0.022(2)	0.032(3)	0.029(3)	0.004(2)	0.008(2)	0.013(2)
C(6)	2i	1.0742(6)	0.8416(5)	0.4856(3)	0.022(2)	0.027(3)	0.028(2)	0.001(2)	0.003(2)	0.008(2)
C(7)	2i	0.4110(6)	0.1718(5)	0.0249(3)	0.028(2)	0.029(3)	0.025(2)	-0.002(2)	-0.002(2)	0.006(2)
C(8)	2i	0.5082(6)	0.2439(5)	0.3236(3)	0.023(2)	0.026(2)	0.025(2)	-0.006(2)	0.003(2)	0.009(2)
C(9)	2i	1.0802(6)	0.4828(5)	0.1255(3)	0.023(2)	0.034(3)	0.021(2)	0.005(2)	0.007(2)	0.010(2)
C(10)	2i	1.1480(5)	0.4375(4)	0.0498(3)	0.019(2)	0.021(2)	0.016(2)	0.007(2)	0.008(2)	0.006(2)
C(11)	2i	1.2985(7)	0.4962(6)	0.0265(4)	0.036(3)	0.052(4)	0.034(3)	0.015(3)	0.019(2)	0.018(3)
C(12)	2i	0.2486(9)	0.0372(6)	-0.0901(5)	0.067(5)	0.030(3)	0.055(4)	0.007(3)	-0.037(4)	-0.015(3)
C(13)	2i	0.3571(1)	0.1137(9)	-0.1143(5)	0.090(6)	0.089(6)	0.032(4)	0.046(5)	0.016(4)	0.022(4)
C(14)	2i	1.1148(9)	0.9658(7)	0.6240(4)	0.070(4)	0.049(4)	0.025(3)	0.021(3)	0.009(3)	0.011(3)
C(15)	2i	1.0049(6)	0.8660(6)	0.5604(4)	0.030(3)	0.052(4)	0.029(3)	0.006(2)	0.009(2)	0.021(3)
C(16)	2i	0.4988(5)	0.2469(5)	0.1119(3)	0.020(2)	0.027(2)	0.024(2)	0.003(2)	0.003(2)	0.008(2)
C(17)	2i	0.6041(5)	0.3277(5)	0.4058(3)	0.020(2)	0.026(2)	0.023(2)	-0.001(2)	0.003(2)	0.009(2)
C(18)	2i	0.4577(6)	0.1995(5)	-0.0434(3)	0.026(2)	0.041(3)	0.019(2)	0.000(2)	0.004(2)	0.017(2)
C(19)	2i	0.9292(7)	0.2997(5)	0.0487(3)	0.035(3)	0.032(3)	0.026(3)	0.003(2)	0.005(2)	0.004(2)
C(20)	2i	1.2447(8)	0.9957(6)	0.5869(4)	0.055(4)	0.031(3)	0.033(3)	-0.012(3)	-0.013(3)	0.006(2)

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References

- Benson, M. T.; Cundari, T. R.; Saunders, L. C.; Sommerer, S. O.: Synthesis, structure, computational studies and magnetic properties of a ten-coordinated gadolinium(III) complex. *Inorg. Chim. Acta* **258** (1997) 127-130.
- Sheldrick, G. M.: SHELXS-86. A direct methods program for crystal structure determination. In: *Crystallographic Computing 3* (Ed. G. M. Sheldrick, C. Krüger, R. Goddard), pp. 175-189. Oxford University Press 1985.
- Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
- Johnson, C. K.: ORTEP-II. A Fortran Thermal-Ellipsoid Plot Program. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA 1976.
- Farrugia, L. J.: WinGX suite for small molecule single-crystal crystallography. *J. Appl. Crystallogr.* **32** (1999) 837-838.
- Spek, A. L.: PLATON. A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands 1998.