Crystal structure of tris(dibenzoylmethanato)-[(*R*,*R*)-6,6-dimethyl-3-pyridin-2-yl-5,6,7,8-tetrahydro-5,7-methanoisoquinoline)]-gadolinium(III), $Gd(C_{15}H_{11}O_2)_3(C_{17}H_{18}N_2)$

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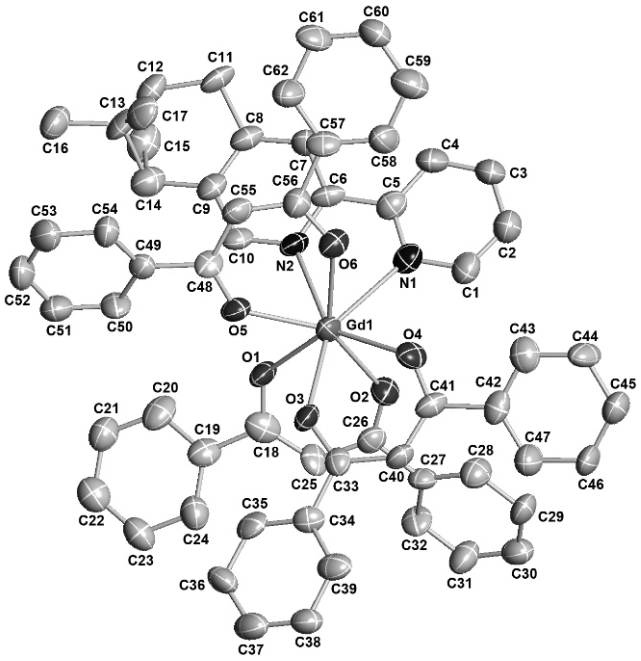

Abstract

$C_{62}H_{51}GdN_2O_6$, monoclinic, $P2_1$ (no. 4), a = 9.504(2) Å, b = 20.748(5) Å, c = 12.704(3) Å, β = 92.432(4)°, V = 2502.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.052, $wR_{ref}(F^2)$ = 0.118, T = 298 K.

Source of material

The chiral ligand (*R*,*R*)-6,6-dimethyl-3-pyridin-2-yl-5,6,7,8-tetrahydro-5,7-methanoiso- quinoline was prepared by the procedures [1] and $Gd(dbm)_3 \cdot 2H_2O$ was synthesized according to [2]. A solution of $Gd(dbm)_3 \cdot 2H_2O$ (86 mg, 0.1 mmol) in ethanol (10 mL) was added to a solution of chiral ligand (25 mg, 0.1 mmol) in acetone (10 mL). The mixture was stirred 10 minutes and kept at RT. Yellow single crystals of title complex suitable for X-ray analysis were obtained in 73 % yield by slow evaporation of the solvent over two weeks.

Experimental details

H atoms were included in calculated positions and treated as riding atoms with d(C—H) = 0.93 (aromatic), 0.97 (methylene) or 0.96 (methyl) Å and U_{iso}(H) = 1.2 or 1.5 U_{eq}(C). The Flack parameter is 0.02(1).

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Discussion

Chiral lanthanide complexes have attracted considerable attention of research in the field of coordination chemistry, material science and life science due to their diverse applications in asymmetric catalysis, enantioselective synthesis, medical diagnotic and therapy [3-7]. Among them, the Gd-based complexes are commonly used as chiral shift reagents for resolving NMR spectra [8].

The introduction of the chiral bipyridine derivative ligand results in the chirality of the title compound, which crystallizes with space group $P2_1$. The chirality is dominated by the two centers C12 and C14 of the bipyridine derivative. the Gd(III) ion is coordinated by six oxygen atoms from three β-diketonate ligands and two nitrogen atoms of chiral pinene bipyridine. The arrangement of O_6N_2 donors can be best approximated as a distorted square antiprism. The bond lengths d(Gd—O) are in the range of 2.328(5) - 2.386(7) Å and d(Gd—N) are 2.574(5) and 2.599(5) Å, respectively. The O3, O4, O5, O6 (bottom plane) and O1, O2, N1, N2 atoms (top plane) comprise the two square-basic planes of the antiprism with mean deviations of 0.072(3) and 0.113(3) Å from each plane, their dihedral angle is 1.7(2)°.

The present compound was synthesized from the starting materials (*R*,*R*)-(–)-6,6-dimethyl-3-pyridin-2-yl-5,6,7,8-tetrahydro-5,7- methanoisoquinoline, while the reported compound was obtained from (*S*,*S*)-(–)-6,6-dimethyl-3-pyridin-2-yl-5,6,7,8-tetrahydro-5,7- methanoisoquinoline. They are a pair of enantiomers, but the synthetic pathways are different [9,10].

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.22 × 0.24 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.81 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13499, 8459
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7308
$N(param)_{refined}$:	642
Programs:	SHELXS-97, SHELXL-97 [11]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	2*a*	0.7362	0.6454	–0.0679	0.066
H(2)	2*a*	0.5965	0.6692	–0.2112	0.076
H(3)	2*a*	0.3914	0.7256	–0.1893	0.072
H(4)	2*a*	0.3287	0.7545	–0.0245	0.075
H(7)	2*a*	0.2849	0.7803	0.1272	0.058

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(10)	2*a*	0.5710	0.6980	0.3886	0.048
H(11A)	2*a*	0.1908	0.8570	0.2885	0.062
H(11B)	2*a*	0.0958	0.7949	0.2890	0.062
H(12)	2*a*	0.1010	0.8407	0.4640	0.061
H(14)	2*a*	0.4213	0.7396	0.5297	0.072
H(15A)	2*a*	0.1600	0.7158	0.4330	0.079
H(15B)	2*a*	0.1646	0.7436	0.5508	0.079
H(16A)	2*a*	0.2626	0.8910	0.6129	0.094
H(16B)	2*a*	0.4055	0.8552	0.6375	0.094
H(16C)	2*a*	0.2628	0.8175	0.6418	0.094
H(17A)	2*a*	0.5060	0.8838	0.4721	0.090
H(17B)	2*a*	0.3727	0.9252	0.4406	0.090
H(17C)	2*a*	0.4237	0.8713	0.3645	0.090
H(20)	2*a*	0.6767	0.6086	0.5168	0.074
H(21)	2*a*	0.6794	0.5857	0.6957	0.072
H(22)	2*a*	0.8407	0.5154	0.7655	0.072
H(23)	2*a*	0.9800	0.4531	0.6560	0.066
H(24)	2*a*	0.9753	0.4767	0.4753	0.069
H(25)	2*a*	0.8889	0.4766	0.3163	0.056
H(28)	2*a*	0.9207	0.5209	–0.0120	0.066
H(29)	2*a*	0.9852	0.4354	–0.1205	0.066
H(30)	2*a*	0.9722	0.3320	–0.0585	0.067
H(31)	2*a*	0.8940	0.3102	0.1075	0.073

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(32)	2*a*	0.8333	0.3956	0.2160	0.058
H(35)	2*a*	1.1168	0.5995	0.4161	0.060
H(36)	2*a*	1.2827	0.5509	0.5335	0.067
H(37)	2*a*	1.4865	0.5095	0.4718	0.072
H(38)	2*a*	1.5415	0.5206	0.2987	0.060
H(39)	2*a*	1.3777	0.5706	0.1840	0.065
H(40)	2*a*	1.2151	0.5915	0.0812	0.053
H(43)	2*a*	0.9712	0.7172	–0.1340	0.067
H(44)	2*a*	1.0197	0.7071	–0.3116	0.068
H(45)	2*a*	1.1670	0.6274	–0.3691	0.072
H(46)	2*a*	1.2629	0.5534	–0.2486	0.070
H(47)	2*a*	1.2111	0.5589	–0.0711	0.074
H(50)	2*a*	0.7932	0.7276	0.5227	0.063
H(51)	2*a*	0.7805	0.7455	0.6993	0.073
H(52)	2*a*	0.7843	0.8514	0.7638	0.073
H(53)	2*a*	0.8028	0.9355	0.6535	0.075
H(54)	2*a*	0.8059	0.9181	0.4733	0.059
H(55)	2*a*	0.7187	0.8930	0.3146	0.068
H(58)	2*a*	0.7270	0.8526	–0.0225	0.074
H(59)	2*a*	0.5994	0.9220	–0.1354	0.084
H(60)	2*a*	0.4485	0.9981	–0.0673	0.069
H(61)	2*a*	0.4377	1.0083	0.1142	0.070
H(62)	2*a*	0.5598	0.9380	0.2264	0.073

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*a*	0.6522(9)	0.6673(4)	–0.0586(6)	0.068(4)	0.045(6)	0.052(4)	0.006(3)	0.004(3)	–0.008(3)
C(2)	2*a*	0.5706(7)	0.6816(7)	–0.1444(5)	0.068(4)	0.071(5)	0.051(3)	0.008(7)	0.002(3)	–0.008(7)
C(3)	2*a*	0.4491(9)	0.7148(4)	–0.1310(6)	0.069(5)	0.059(5)	0.051(4)	0.028(4)	–0.009(4)	0.001(4)
C(4)	2*a*	0.412(1)	0.7320(4)	–0.0340(7)	0.070(5)	0.058(5)	0.058(5)	0.031(4)	0.001(4)	0.006(4)
C(5)	2*a*	0.4998(7)	0.7156(4)	0.0512(6)	0.042(3)	0.044(4)	0.056(4)	–0.003(3)	0.008(3)	–0.001(3)
C(6)	2*a*	0.4608(6)	0.7304(3)	0.1608(6)	0.026(3)	0.032(4)	0.070(4)	0.005(2)	0.004(3)	0.004(3)
C(7)	2*a*	0.3424(7)	0.7638(4)	0.1818(6)	0.041(3)	0.055(5)	0.049(4)	0.008(3)	–0.002(3)	–0.001(3)
C(8)	2*a*	0.3086(9)	0.7729(4)	0.2860(7)	0.045(4)	0.038(5)	0.063(5)	0.014(3)	0.019(4)	0.002(3)
C(9)	2*a*	0.3964(7)	0.7493(3)	0.3639(6)	0.049(4)	0.033(4)	0.054(4)	0.005(3)	0.010(3)	–0.004(3)
C(10)	2*a*	0.5137(7)	0.7160(3)	0.3351(5)	0.039(3)	0.028(3)	0.052(4)	0.008(3)	0.009(3)	0.005(3)
C(11)	2*a*	0.1828(7)	0.8139(4)	0.3171(6)	0.044(4)	0.043(5)	0.069(5)	0.016(3)	0.024(3)	–0.005(4)
C(12)	2*a*	0.1811(8)	0.8170(4)	0.4372(6)	0.054(4)	0.042(5)	0.057(4)	0.002(3)	0.016(3)	–0.017(4)
C(13)	2*a*	0.3209(9)	0.8339(4)	0.4906(8)	0.059(5)	0.043(5)	0.070(6)	0.008(4)	0.017(4)	–0.026(4)
C(14)	2*a*	0.3607(9)	0.7599(4)	0.4749(7)	0.056(4)	0.056(5)	0.069(5)	0.010(4)	0.012(4)	0.006(4)
C(15)	2*a*	0.197(1)	0.7491(5)	0.4801(7)	0.070(5)	0.062(6)	0.069(5)	–0.013(4)	0.021(4)	–0.007(4)
C(16)	2*a*	0.312(1)	0.8510(5)	0.6063(6)	0.077(5)	0.057(5)	0.055(4)	0.008(4)	0.017(4)	–0.008(4)
C(17)	2*a*	0.4146(8)	0.8832(5)	0.4369(6)	0.058(4)	0.058(6)	0.064(5)	–0.002(4)	–0.006(4)	–0.030(4)
C(18)	2*a*	0.815(1)	0.5608(5)	0.3649(8)	0.038(4)	0.051(6)	0.053(6)	–0.008(4)	0.008(4)	–0.002(5)
C(19)	2*a*	0.8280(9)	0.5465(4)	0.4793(8)	0.048(5)	0.036(5)	0.060(5)	–0.006(3)	0.010(4)	0.004(4)
C(20)	2*a*	0.739(1)	0.5780(4)	0.5448(8)	0.081(6)	0.035(5)	0.071(6)	0.001(4)	0.026(5)	–0.006(4)
C(21)	2*a*	0.741(1)	0.5648(5)	0.6524(7)	0.068(6)	0.060(6)	0.054(5)	0.004(5)	0.014(4)	–0.004(4)
C(22)	2*a*	0.834(1)	0.5216(7)	0.6930(8)	0.062(5)	0.064(7)	0.052(6)	–0.019(5)	0.002(4)	0.004(4)
C(23)	2*a*	0.9216(9)	0.4853(4)	0.6279(6)	0.059(4)	0.057(5)	0.048(4)	–0.006(4)	–0.011(3)	0.011(4)
C(24)	2*a*	0.9176(9)	0.4992(4)	0.5198(6)	0.074(5)	0.055(5)	0.045(4)	–0.001(4)	0.000(4)	–0.002(4)
C(25)	2*a*	0.8528(8)	0.5156(4)	0.2910(5)	0.063(5)	0.042(4)	0.036(3)	–0.002(3)	0.010(3)	0.012(3)
C(26)	2*a*	0.8416(7)	0.5234(4)	0.1817(5)	0.032(3)	0.046(4)	0.049(4)	0.005(3)	0.007(3)	–0.004(3)
C(27)	2*a*	0.8745(7)	0.4658(3)	0.1126(5)	0.043(3)	0.033(4)	0.044(3)	0.013(3)	0.001(3)	0.005(3)
C(28)	2*a*	0.9171(8)	0.4787(4)	0.0122(6)	0.063(5)	0.045(5)	0.056(4)	0.001(4)	0.010(3)	0.004(4)
C(29)	2*a*	0.9549(8)	0.4275(4)	–0.0530(6)	0.059(4)	0.061(5)	0.046(4)	0.016(4)	0.011(3)	–0.016(4)
C(30)	2*a*	0.9464(8)	0.3660(4)	–0.0157(6)	0.057(4)	0.047(5)	0.062(5)	0.013(3)	–0.005(4)	–0.006(4)
C(31)	2*a*	0.9004(9)	0.3526(4)	0.0842(6)	0.079(5)	0.047(5)	0.058(4)	0.008(4)	0.019(4)	–0.006(4)
C(32)	2*a*	0.8642(9)	0.4035(3)	0.1488(6)	0.071(5)	0.021(3)	0.053(4)	–0.004(3)	–0.001(3)	–0.004(3)
C(33)	2*a*	1.1297(7)	0.6234(3)	0.2145(5)	0.051(4)	0.028(4)	0.039(3)	–0.003(3)	0.002(3)	–0.001(3)
C(34)	2*a*	1.2356(8)	0.5889(3)	0.2889(6)	0.033(3)	0.034(4)	0.053(4)	–0.007(3)	0.004(3)	0.003(3)
C(35)	2*a*	1.2018(9)	0.5839(4)	0.3928(6)	0.061(4)	0.028(4)	0.060(4)	0.006(3)	0.004(4)	–0.010(3)
C(36)	2*a*	1.301(1)	0.5543(5)	0.4623(7)	0.064(5)	0.053(6)	0.049(5)	0.008(4)	–0.018(4)	0.001(4)
C(37)	2*a*	1.4236(9)	0.5304(4)	0.4252(7)	0.058(5)	0.049(5)	0.072(5)	0.013(4)	–0.018(4)	–0.015(4)
C(38)	2*a*	1.4567(8)	0.5361(4)	0.3226(6)	0.050(4)	0.042(4)	0.058(4)	0.013(3)	–0.005(3)	–0.002(3)
C(39)	2*a*	1.3583(9)	0.5662(4)	0.2548(7)	0.056(4)	0.038(4)	0.068(5)	0.004(3)	–0.010(4)	–0.009(4)
C(40)	2*a*	1.1428(7)	0.6173(4)	0.1048(5)	0.039(3)	0.047(4)	0.048(4)	0.014(3)	0.008(3)	–0.008(3)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(41)	2*a*	1.0563(7)	0.6468(3)	0.0312(6)	0.041(3)	0.032(4)	0.058(4)	0.008(3)	0.016(3)	0.004(3)
C(42)	2*a*	1.0884(8)	0.6382(4)	–0.0841(6)	0.052(4)	0.048(4)	0.047(4)	–0.008(3)	0.008(3)	–0.014(3)
C(43)	2*a*	1.0288(7)	0.6841(7)	–0.1567(5)	0.060(3)	0.056(4)	0.052(3)	–0.006(6)	0.000(3)	–0.010(7)
C(44)	2*a*	1.0594(7)	0.6780(6)	–0.2631(5)	0.066(4)	0.050(5)	0.055(3)	0.022(5)	0.014(3)	0.020(5)
C(45)	2*a*	1.1467(9)	0.6301(5)	–0.2983(6)	0.064(5)	0.068(6)	0.048(4)	0.012(4)	0.013(4)	–0.013(4)
C(46)	2*a*	1.2039(9)	0.5858(4)	–0.2256(6)	0.072(5)	0.065(6)	0.038(3)	0.022(4)	0.015(3)	–0.008(3)
C(47)	2*a*	1.174(1)	0.5893(4)	–0.1185(6)	0.073(5)	0.067(6)	0.045(4)	0.015(4)	0.010(4)	0.004(4)
C(48)	2*a*	0.7997(8)	0.8068(4)	0.3627(7)	0.040(4)	0.025(4)	0.051(5)	–0.009(3)	0.009(3)	–0.002(4)
C(49)	2*a*	0.7961(8)	0.8212(4)	0.4791(7)	0.031(3)	0.041(5)	0.039(4)	0.005(3)	–0.005(3)	–0.006(3)
C(50)	2*a*	0.792(1)	0.7695(4)	0.5484(7)	0.085(6)	0.020(4)	0.053(4)	0.011(3)	0.000(4)	0.002(3)
C(51)	2*a*	0.786(1)	0.7800(5)	0.6531(8)	0.065(5)	0.056(6)	0.062(5)	0.022(4)	0.004(4)	0.004(4)
C(52)	2*a*	0.789(1)	0.8441(7)	0.6918(7)	0.065(6)	0.075(8)	0.042(5)	0.016(5)	0.008(4)	–0.001(4)
C(53)	2*a*	0.7982(9)	0.8938(5)	0.6269(7)	0.062(5)	0.066(6)	0.058(5)	0.011(4)	–0.011(4)	–0.014(4)
C(54)	2*a*	0.8009(8)	0.8832(4)	0.5190(5)	0.053(4)	0.058(5)	0.037(3)	0.004(3)	0.004(3)	–0.008(3)
C(55)	2*a*	0.7453(8)	0.8530(5)	0.2893(6)	0.051(4)	0.068(6)	0.051(4)	0.013(4)	0.009(3)	0.004(4)
C(56)	2*a*	0.7300(8)	0.8417(4)	0.1844(6)	0.048(4)	0.049(5)	0.047(4)	0.001(3)	0.003(3)	–0.004(3)
C(57)	2*a*	0.6534(7)	0.8884(3)	0.1128(6)	0.047(3)	0.029(4)	0.065(4)	0.000(3)	0.002(3)	0.009(3)
C(58)	2*a*	0.6674(9)	0.8834(5)	0.0048(6)	0.060(5)	0.077(6)	0.049(4)	0.025(4)	0.010(3)	0.009(4)
C(59)	2*a*	0.591(1)	0.9252(5)	–0.0630(8)	0.067(5)	0.072(7)	0.070(6)	0.012(5)	–0.009(4)	0.014(5)
C(60)	2*a*	0.5017(8)	0.9712(4)	–0.0226(6)	0.056(4)	0.059(5)	0.055(4)	0.012(4)	–0.012(3)	0.001(4)
C(61)	2*a*	0.4937(9)	0.9764(4)	0.0862(7)	0.058(4)	0.051(5)	0.065(5)	0.014(4)	0.009(4)	0.027(4)
C(62)	2*a*	0.5679(9)	0.9347(4)	0.1539(7)	0.070(5)	0.056(5)	0.057(4)	0.018(4)	0.009(4)	0.008(4)
Gd(1)	2*a*	0.80811(3)	0.68252(2)	0.19401(2)	0.0407(2)	0.0530(2)	0.0384(1)	0.0115(2)	0.00700(9)	–0.0005(2)
N(1)	2*a*	0.6189(5)	0.6829(5)	0.0401(4)	0.049(2)	0.043(3)	0.054(3)	0.003(4)	0.005(2)	–0.010(5)
N(2)	2*a*	0.5514(6)	0.7077(3)	0.2362(4)	0.045(3)	0.036(3)	0.049(3)	0.011(2)	0.014(2)	0.002(2)
O(1)	2*a*	0.7656(6)	0.6178(2)	0.3393(4)	0.060(3)	0.035(3)	0.044(3)	0.015(2)	0.017(2)	–0.001(2)
O(2)	2*a*	0.8044(7)	0.5747(3)	0.1347(5)	0.054(3)	0.042(3)	0.041(3)	0.000(2)	0.004(2)	0.011(3)
O(3)	2*a*	1.0343(5)	0.6546(2)	0.2558(3)	0.051(3)	0.040(3)	0.038(2)	0.010(2)	0.011(2)	–0.006(2)
O(4)	2*a*	0.9537(4)	0.6819(4)	0.0490(3)	0.056(2)	0.045(2)	0.044(2)	0.007(4)	0.007(2)	0.018(4)
O(5)	2*a*	0.8418(6)	0.7508(2)	0.3383(4)	0.048(3)	0.034(3)	0.052(3)	0.011(2)	0.000(2)	–0.006(2)
O(6)	2*a*	0.7761(6)	0.7916(3)	0.1387(5)	0.050(3)	0.047(4)	0.050(4)	0.001(3)	0.012(2)	0.001(3)

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