Crystal structure of [(*R*,*R*)-6,6-dimethyl-3-pyridin-2-yl-5,6,7,8-tetrahydro-5,7-methanoisoquinoline]-tris[4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dionato]dysprosium(III), $Dy(C_{17}H_{18}N_2)(C_8H_4O_2SF_3)_3$

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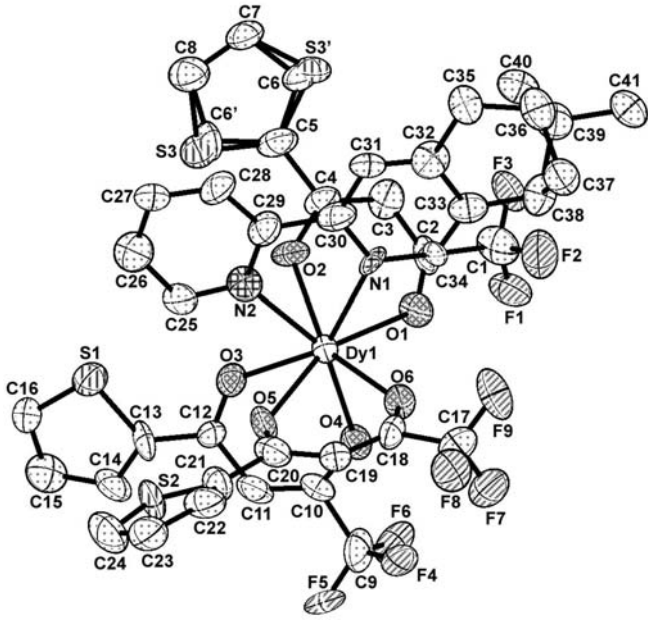

Abstract

$C_{41}H_{30}DyF_9N_2O_6S_3$, monoclinic, $P2_1$ (no. 4), a = 10.174(2) Å, b = 19.018(4) Å, c = 12.037(2) Å, β = 113.742(3)°, V = 2131.9 Å^3, Z = 2, $R_{gt}(F)$ = 0.048, $wR_{ref}(F^2)$ = 0.112, T = 291 K.

Source of material

The chiral ligand was prepared by the documented procedures [1] and $Dy(tta)_3 \cdot 2H_2O$ (tta = 4,4,4,-trifluoro-1-(2-thienyl)butane-1,3-dionato) was synthesized according to literature method [2]. A solution of $Dy(tta)_3 \cdot 2H_2O$ (87 mg, 0.1 mmol) in ethanol (5 mL) was added to a solution of chiral ligand (*R*,*R*)-6,6-dimethyl-3-pyridin-2-yl-5,6,7,8-tetrahydro-5,7-methanoisoquinoline (25 mg, 0.1 mmol) in acetone (5 mL). The mixture was kept at RT. Yellow single crystals of title complex, suitable for X-ray analysis, were obtained in 73 % yield by slow evaporation of solvents over two weeks. Elemental analysis — found: C, 45.36 %; H, 3.02 %; N, 2.91 %; calculated for $C_{41}H_{30}DyF_9N_2O_6S_3$: C, 45.75 %; H, 2.81 %; N, 2.60 %.

Experimental details

H atoms were included in calculated positions and treated as riding atoms with d(C—H) = 0.93 Å (aromatic), 0.98 Å (tertiary), 0.97 Å (methylene) or 0.96 Å (methyl) and U_{iso}(H) = 1.2 or 1.5 U_{eq}(C). The Flack parameter is 0.03(2).

Discussion

Over the last decades, chiral complexes have been an active area of research in coordination chemistry due to their diverse application in asymmetric catalysis, enantioselective synthesis, bioinorganic and supramolecular chemistry [3-6]. An effective and facile method to prepare such kind of complexes is the generating of chiral motifs in the target molecule. Based on this strategy, as a continuance of our research [7], we employed a chiral ligand (*R*,*R*)-6,6-dimethyl-3-pyridin-2-yl-5,6,7,8-tetrahydro-5,7-methanoisoquinoline to react with $Dy(tta)_3 \cdot 2H_2O$. Subsequently, the enantiomerically pure title compound was obtained.

The unit cell of the title crystal structure contains two mononuclear neutral complexes. Each molecule is formed by three β-diketonate anions, a chiral bipyridine derivative ligand and an eight-coordinated Dy(III) cation. The Dy(III) ion is coordinated with six O atoms from three β-diketonate ligands. The other two coordination sites are occupied by two N atoms of a chiral bipyridine derivative. The Dy—O bond lengthes range from 2.344(6) to 2.405(6) Å, while the Dy—N bond lengths are 2.527(7) and 2.567(7) Å. Eight bonds with different lengths give rise to a strongly distorted square antiprismatic environment of the Dy(III) ion. The two square planes are defined by O5, O6, N1, N2 and O1, O2, O3, O4 with the mean deviations of 0.024 and 0.030 Å, respectively. The dihedral angle is 3.38(1)°.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.24 × 0.26 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	19.87 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11457, 6171
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5394
$N(param)_{refined}$:	569
Programs:	SHELXS-97, SHELXL-97, SHELXTL [8]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(3A)	2*a*		0.1172	0.8961	0.4104	0.064
C(6)	2*a*	0.73(2)	0.162(3)	0.760(2)	0.498(3)	0.06(1)
H(6)	2*a*	0.73	0.2260	0.7988	0.5344	0.069

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Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(7)	2*a*		0.2467	0.6664	0.6071	0.065
H(8)	2*a*		0.0410	0.5997	0.4737	0.064
C(6')	2*a*	0.27	–0.006(7)	0.689(4)	0.355(7)	0.06(2)
H(6D)	2*a*	0.27	–0.0814	0.6737	0.2832	0.070
H(11A)	2*a*		–0.6052	0.8699	–0.2320	0.064
H(14A)	2*a*		–0.7689	0.7951	–0.1946	0.068
H(15A)	2*a*		–0.8856	0.6877	–0.1712	0.062
H(16)	2*a*		–0.7065	0.5984	–0.0595	0.077
H(19A)	2*a*		–0.0763	0.8306	–0.3791	0.057
H(22A)	2*a*		–0.1465	0.7176	–0.4767	0.059
H(23A)	2*a*		–0.3231	0.6425	–0.6138	0.073
H(24)	2*a*		–0.5114	0.6145	–0.5321	0.082
H(25A)	2*a*		–0.2215	0.6770	–0.0661	0.063
H(26A)	2*a*		–0.1323	0.5602	–0.0062	0.064
H(27A)	2*a*		0.0974	0.5384	0.1110	0.064
H(28A)	2*a*		0.2561	0.6301	0.1537	0.066

Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(31A)	2*a*		0.4058	0.7232	0.2052	0.049
H(34A)	2*a*		0.1820	0.9311	0.0969	0.044
H(35A)	2*a*		0.6302	0.7986	0.3422	0.055
H(35B)	2*a*		0.6480	0.7921	0.2192	0.055
H(36A)	2*a*		0.7748	0.8931	0.3268	0.066
H(37A)	2*a*		0.5930	0.9046	0.0925	0.062
H(37B)	2*a*		0.6678	0.9744	0.1652	0.062
H(38A)	2*a*		0.4322	0.9936	0.1669	0.055
H(40A)	2*a*		0.6095	0.9170	0.5056	0.071
H(40B)	2*a*		0.4927	0.8703	0.4081	0.071
H(40C)	2*a*		0.4563	0.9478	0.4301	0.071
H(41A)	2*a*		0.7234	1.0069	0.4686	0.080
H(41B)	2*a*		0.5905	1.0494	0.3792	0.080
H(41C)	2*a*		0.7137	1.0272	0.3393	0.080
S(3)	2*a*	0.73	–0.0310(6)	0.6811(3)	0.3283(6)	0.043(2)
S(3')	2*a*	0.27	0.180(2)	0.770(1)	0.515(2)	0.048(5)

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*a*		0.087(1)	1.0167(6)	0.302(1)	0.057(6)	0.042(6)	0.052(7)	0.001(5)	0.018(6)	–0.019(5)
C(2)	2*a*		0.025(1)	0.9434(6)	0.246(1)	0.045(6)	0.041(6)	0.044(6)	–0.004(5)	0.010(5)	–0.013(5)
C(3)	2*a*		0.061(2)	0.8876(7)	0.329(1)	0.083(9)	0.049(8)	0.038(7)	–0.008(7)	0.035(7)	–0.010(6)
C(4)	2*a*		0.015(1)	0.8205(7)	0.292(1)	0.070(7)	0.041(6)	0.028(6)	0.008(6)	0.017(5)	–0.003(5)
C(5)	2*a*		0.050(1)	0.7588(7)	0.3795(9)	0.052(6)	0.057(7)	0.030(5)	0.001(5)	0.020(5)	0.007(5)
C(7)	2*a*		0.175(1)	0.6906(7)	0.547(1)	0.057(6)	0.064(8)	0.043(6)	0.023(6)	0.021(5)	0.010(6)
C(8)	2*a*		0.072(1)	0.6473(7)	0.459(1)	0.056(6)	0.053(7)	0.055(7)	0.018(6)	0.027(6)	0.011(6)
C(9)	2*a*		–0.497(1)	0.9878(7)	–0.242(1)	0.035(5)	0.048(7)	0.062(7)	0.001(5)	0.014(5)	0.021(6)
C(10)	2*a*		–0.431(1)	0.9233(6)	–0.160(1)	0.033(5)	0.049(7)	0.042(6)	–0.006(5)	0.003(4)	0.012(5)
C(11)	2*a*		–0.513(1)	0.8685(6)	–0.172(1)	0.039(5)	0.06(1)	0.047(6)	–0.014(5)	0.002(4)	0.012(5)
C(12)	2*a*		–0.469(1)	0.8060(6)	–0.0982(9)	0.037(5)	0.044(6)	0.026(5)	–0.008(4)	0.008(4)	0.000(4)
C(13)	2*a*		–0.574(1)	0.7529(6)	–0.109(1)	0.040(5)	0.029(5)	0.053(6)	–0.008(4)	0.013(4)	–0.012(5)
C(14)	2*a*		–0.718(1)	0.7553(8)	–0.156(1)	0.036(6)	0.061(8)	0.054(7)	–0.010(6)	–0.002(5)	0.014(6)
C(15)	2*a*		–0.787(1)	0.6938(7)	–0.142(1)	0.039(6)	0.068(9)	0.054(7)	–0.010(6)	0.024(5)	0.004(6)
C(16)	2*a*		–0.684(1)	0.6428(8)	–0.079(1)	0.051(7)	0.059(8)	0.065(8)	–0.023(6)	0.005(6)	0.015(6)
C(17)	2*a*		0.064(1)	0.9430(7)	–0.269(1)	0.064(7)	0.048(7)	0.037(6)	–0.016(6)	0.016(5)	0.014(5)
C(18)	2*a*		–0.030(1)	0.8921(6)	–0.232(1)	0.055(6)	0.046(7)	0.036(6)	–0.018(5)	0.018(5)	–0.003(5)
C(19)	2*a*		–0.096(1)	0.8373(6)	–0.311(1)	0.041(4)	0.038(9)	0.057(6)	0.006(5)	0.013(4)	–0.004(5)
C(20)	2*a*		–0.192(1)	0.7905(7)	–0.288(1)	0.050(6)	0.051(7)	0.048(7)	–0.015(5)	0.002(5)	–0.009(6)
C(21)	2*a*		–0.265(1)	0.7379(6)	–0.382(1)	0.035(5)	0.043(6)	0.051(6)	–0.004(4)	0.013(4)	–0.020(5)
C(22)	2*a*		–0.232(1)	0.7074(6)	–0.469(1)	0.054(6)	0.050(7)	0.038(6)	0.007(5)	0.013(5)	–0.008(5)
C(23)	2*a*		–0.327(2)	0.6620(7)	–0.544(1)	0.09(1)	0.046(7)	0.037(6)	–0.004(7)	0.018(6)	–0.013(5)
C(24)	2*a*		–0.439(2)	0.6480(8)	–0.500(1)	0.065(7)	0.061(9)	0.063(8)	–0.017(7)	0.010(6)	–0.035(7)
C(25)	2*a*		–0.125(1)	0.6687(6)	–0.020(1)	0.061(7)	0.032(6)	0.041(6)	–0.004(5)	–0.003(5)	–0.014(5)
C(26)	2*a*		–0.068(1)	0.5976(7)	0.018(1)	0.059(7)	0.035(6)	0.063(8)	0.004(5)	0.022(6)	–0.009(5)
C(27)	2*a*		0.066(1)	0.5838(6)	0.085(1)	0.070(7)	0.036(6)	0.032(6)	–0.005(5)	–0.002(5)	0.008(4)
C(28)	2*a*		0.158(1)	0.6389(6)	0.113(1)	0.059(7)	0.033(6)	0.064(8)	0.003(5)	0.016(6)	0.013(5)
C(29)	2*a*		0.112(1)	0.7092(6)	0.083(1)	0.049(6)	0.031(6)	0.050(6)	0.002(5)	0.016(5)	0.002(5)
C(30)	2*a*		0.214(1)	0.7704(6)	0.117(1)	0.041(5)	0.029(6)	0.047(6)	0.006(4)	0.023(5)	0.000(5)
C(31)	2*a*		0.364(1)	0.7668(6)	0.1774(9)	0.044(6)	0.039(6)	0.031(5)	0.007(5)	0.005(4)	0.013(4)
C(32)	2*a*		0.446(1)	0.8205(6)	0.196(1)	0.039(5)	0.046(6)	0.061(7)	0.014(5)	0.030(5)	0.019(5)
C(33)	2*a*		0.373(1)	0.8867(6)	0.157(1)	0.031(5)	0.034(6)	0.071(8)	0.006(5)	0.022(5)	0.004(6)
C(34)	2*a*		0.227(1)	0.8876(6)	0.1101(9)	0.030(5)	0.029(6)	0.032(5)	0.006(4)	–0.007(4)	–0.004(4)
C(35)	2*a*		0.606(1)	0.8204(7)	0.264(1)	0.033(5)	0.051(6)	0.055(7)	0.013(5)	0.019(5)	–0.001(5)
C(36)	2*a*		0.670(1)	0.8915(7)	0.282(1)	0.047(7)	0.062(9)	0.062(8)	–0.003(6)	0.029(6)	–0.010(6)
C(37)	2*a*		0.613(1)	0.9328(7)	0.165(1)	0.043(6)	0.053(7)	0.068(8)	–0.009(5)	0.030(6)	–0.008(6)
C(38)	2*a*		0.477(1)	0.9474(6)	0.193(1)	0.045(6)	0.049(7)	0.053(6)	–0.010(5)	0.029(5)	–0.007(5)
C(39)	2*a*		0.580(1)	0.9425(6)	0.333(1)	0.041(5)	0.046(7)	0.059(7)	0.006(5)	0.022(5)	0.003(5)
C(40)	2*a*		0.530(1)	0.9171(7)	0.428(1)	0.036(5)	0.057(7)	0.048(6)	0.003(5)	0.016(5)	–0.003(5)
C(41)	2*a*		0.660(1)	1.0133(7)	0.385(1)	0.036(5)	0.063(8)	0.063(8)	–0.003(5)	0.022(5)	–0.013(6)
Dy(1)	2*a*		–0.12165(4)	0.84819(2)	–0.00602(3)	0.0324(2)	0.0311(2)	0.0319(2)	–0.0074(3)	0.0082(1)	0.0004(3)
F(1)	2*a*		–0.0102(8)	1.0596(4)	0.2666(7)	0.068(4)	0.050(4)	0.053(4)	0.011(4)	–0.003(3)	–0.019(3)
F(2)	2*a*		0.1724(7)	1.0408(4)	0.2570(7)	0.063(4)	0.063(5)	0.068(5)	0.013(4)	0.035(4)	–0.012(4)
F(3)	2*a*		0.1465(7)	1.0197(4)	0.4180(6)	0.059(4)	0.051(4)	0.053(4)	–0.015(3)	–0.004(3)	–0.014(3)
F(4)	2*a*		–0.4088(8)	1.0106(4)	–0.2921(6)	0.066(4)	0.072(5)	0.046(4)	–0.013(4)	0.013(3)	0.022(4)
F(5)	2*a*		–0.6152(7)	0.9774(4)	–0.3300(7)	0.059(4)	0.068(5)	0.064(5)	–0.001(4)	–0.001(3)	0.041(4)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F(6)	2*a*	–0.5062(8)	1.0392(4)	–0.1756(6)	0.076(4)	0.048(4)	0.060(4)	0.002(4)	0.033(4)	0.025(4)
F(7)	2*a*	–0.0067(8)	1.0011(4)	–0.3010(7)	0.065(4)	0.054(4)	0.078(5)	–0.003(3)	0.038(4)	0.018(4)
F(8)	2*a*	0.0883(8)	0.9233(4)	–0.3625(7)	0.069(4)	0.075(5)	0.064(5)	–0.015(4)	0.038(4)	0.005(4)
F(9)	2*a*	0.1826(8)	0.9589(5)	–0.1793(7)	0.051(4)	0.079(6)	0.065(5)	–0.026(4)	0.020(3)	–0.021(4)
N(1)	2*a*	0.1477(8)	0.8321(4)	0.0827(8)	0.035(4)	0.032(6)	0.044(4)	0.003(3)	0.016(3)	0.006(3)
N(2)	2*a*	–0.0264(9)	0.7217(5)	0.0158(8)	0.041(4)	0.036(5)	0.054(5)	0.002(4)	0.027(4)	–0.005(4)
O(1)	2*a*	–0.0395(8)	0.9444(4)	0.1352(7)	0.048(4)	0.037(4)	0.043(4)	0.003(3)	0.013(3)	–0.012(3)
O(2)	2*a*	–0.0817(7)	0.8043(4)	0.1888(6)	0.046(4)	0.048(4)	0.032(4)	0.006(3)	0.018(3)	0.003(3)
O(3)	2*a*	–0.3384(7)	0.7959(4)	–0.0271(7)	0.033(3)	0.033(4)	0.051(4)	0.000(3)	0.016(3)	0.003(3)
O(4)	2*a*	–0.2997(7)	0.9349(4)	–0.0950(7)	0.032(3)	0.038(4)	0.059(5)	–0.003(3)	0.009(3)	0.007(3)
O(5)	2*a*	–0.2249(9)	0.7930(4)	–0.1996(7)	0.058(5)	0.049(5)	0.034(4)	–0.020(4)	0.004(3)	–0.009(3)
O(6)	2*a*	–0.0367(7)	0.9089(4)	–0.1354(6)	0.042(4)	0.050(5)	0.031(4)	–0.012(3)	0.011(3)	0.002(3)
S(1)	2*a*	–0.5140(3)	0.6720(2)	–0.0425(3)	0.042(1)	0.053(2)	0.062(2)	–0.004(1)	0.014(1)	0.019(1)
S(2)	2*a*	–0.4178(3)	0.7026(2)	–0.3790(3)	0.045(1)	0.044(2)	0.047(2)	–0.021(1)	0.012(1)	–0.017(1)

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