Crystal structure of bis(4,5-dihydro-4,4,5,5-tetramethyl-2-(2'-pyridyl-κ*N*)-imidazol-1-oxyl-3-oxide-κ*O*-tris(nitrato-κ^2*O,O'*)europium(III), $C_{24}H_{32}EuN_9O_{13}$

Dong-Jiao Li*

Linyi University, College of Chemistry and Chemical Engineering, Linyi 276005, Shandong Province, P. R.China

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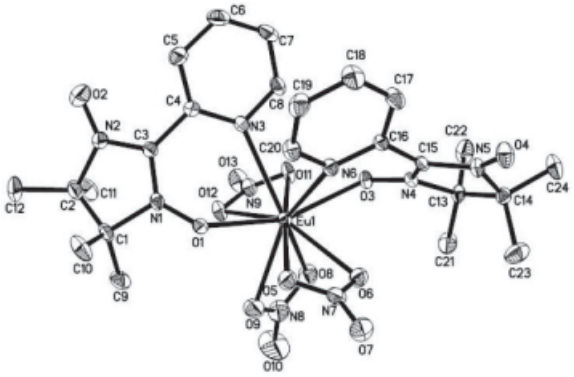

Abstract

$C_{24}H_{32}EuN_9O_{13}$, monoclinic, $P2_1/n$ (no. 14), a = 12.337(4) Å, b = 11.093(4) Å, c = 23.317(7) Å, β = 98.331(5)°, V = 3157.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.0431, $wR_{ref}(F^2)$ = 0.1104, T = 293 K.

Table 1. Data collection and handling.

Crystal:	brown blocks, size 0.08×0.18×0.22 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	20.64 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	52.9°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17733, 6481
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4650
$N(param)_{refined}$:	432
Programs:	SHELX [3]

Source of material

NIT2Py: 2-(2'-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide was prepared by the literature method [1, 2]. The title compound was synthesized by the following procedure. $Eu(NO_3)_3{\cdot}6H_2O$ (0.046 g, 0.2 mmol) and NIT2Py (0.047 g, 0.2 mmol) were dissolved in 10 ml of anhydrous THF. The mixture was stirred at room temperature for four hours and then filtered. The dark brown filtrate was allowed to stand in the dark for one week yielding dark brown crystals. **Elemental Analysis** calcd. for $C_{24}H_{32}N_9O_{13}Eu$ (%): C, 35.70; H, 3.97; N, 15.62. Found (%): C, 35.49; H, 4.05; N, 15.76.

Experimental details

Elemental analysis for carbon, hydrogen and nitrogen were carried out on a Model 240 Perkin-Elmer elemental analyzer. The infrared spectrum was taken on a Shimadzu IR spectrophotometer model 408 in the 4000-600 cm^{-1} regions, using KBr pellets.

* e-mail: lidongjiao@lyu.edu.cn

Discussion

Lanthanide ions which are bound to nitronyl nitroxide radicals have been reported. In title compound, the metal ion is ten-coordinated by two radicals and three nitrate ligands. The radical behaves as a bidentate chelating ligand through one oxygen of nitronyl nitroxide and one nitrogen of pyridyl, while the other oxygen of nitronyl nitroxide remains uncoordinated. The coordination sphere of the Eu atom is completed by the η^2-coordination of the three NO_3^- ligands. The N1–O1 and N5–O3 (coordinated to Eu(III) ion) bond length (1.305(6) Å and 1.299(5) Å) is longer than the N2–O2 and N5–O4 (uncoordinated to Eu(III) ion) bond length (1.271(7) Å and 1.274(5) Å). This is in agreement with the observation that the N–O stretching vibration at 1360cm^{-1} for free radical is shifted to lower frequencies (1320 cm^{-1}) for the complex in IR spectrum. The O(1)N(1)C(3)N(2)O(2) and the O(3)N(4)C(15)N(5)O(4) moieties are almost planar, indicating the easy delocalization of the free electron. The dihedral angles between the nitronyl nitroxide moiety and the pyridyl subsituent are 38.1º and 34.6º for two radicals in the complex, respectively. The Eu–N bond lengths are 2.686(5) Å and 2.736(4) Å, respectively. The Eu–O(NO_3) bond lengths can be classified into two groups: (a) Those with Eu–O bond lengths (Eu–O9, Eu–O6, Eu–O8 and Eu–O11) ranging from 2.482(4) Å to 2.505(4) Å and (b) those with bond lengths of 2.551(4) Å (Eu–O12) and 2.554(4) Å (Eu–O5).

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

Atom	Site	x	y	z	U_{iso}
H(5)	4*e*	0.2382	0.1682	0.1716	0.050
H(6)	4*e*	0.0517	0.1240	0.1554	0.065
H(7)	4*e*	–0.0677	0.2626	0.1078	0.058
H(8)	4*e*	–0.0039	0.4485	0.0859	0.042
H(9A)	4*e*	0.5015	0.5836	0.0837	0.075
H(9B)	4*e*	0.6186	0.5744	0.1199	0.075
H(9C)	4*e*	0.5281	0.6528	0.1427	0.075
H(10A)	4*e*	0.5206	0.5479	0.2349	0.083
H(10B)	4*e*	0.6285	0.4841	0.2230	0.083
H(10C)	4*e*	0.5291	0.4070	0.2370	0.083
H(11A)	4*e*	0.5136	0.2727	0.0447	0.082
H(11B)	4*e*	0.5758	0.3963	0.0494	0.082
H(11C)	4*e*	0.4476	0.3936	0.0432	0.082
H(12A)	4*e*	0.6203	0.2650	0.1918	0.096
H(12B)	4*e*	0.6866	0.3218	0.1461	0.096
H(12C)	4*e*	0.6220	0.2012	0.1320	0.096
H(17)	4*e*	–0.1982	0.5719	0.2132	0.049
H(18)	4*e*	–0.1110	0.4331	0.2786	0.058
H(19)	4*e*	0.0792	0.4199	0.2903	0.055
H(20)	4*e*	0.1717	0.5339	0.2317	0.042
H(21A)	4*e*	–0.0401	0.9510	0.0575	0.081
H(21B)	4*e*	–0.1372	0.9775	0.0080	0.081

Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(21C)	4*e*	–0.0522	0.8761	0.0000	0.081
H(22A)	4*e*	–0.1826	0.7075	–0.0154	0.077
H(22B)	4*e*	–0.2745	0.8061	–0.0198	0.077
H(22C)	4*e*	–0.2763	0.6976	0.0231	0.077
H(23A)	4*e*	–0.2221	1.0169	0.1578	0.084
H(23B)	4*e*	–0.1938	1.0575	0.0973	0.084
H(23C)	4*e*	–0.1067	0.9879	0.1406	0.084
H(24A)	4*e*	–0.3788	0.8023	0.0735	0.072
H(24B)	4*e*	–0.3669	0.9323	0.0488	0.072
H(24C)	4*e*	–0.3836	0.9149	0.1137	0.072

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}
Eu(1)	4*e*	0.18056(2)	0.66130(3)	0.10363(1)	0.0219(2)	0.0276(2)	0.0244(2)	0.0014(1)	0.0019(1)	0.0022(1)
N(1)	4*e*	0.3824(3)	0.4738(4)	0.1504(2)	0.022(2)	0.033(3)	0.026(3)	0.003(2)	0.002(2)	0.010(2)
N(2)	4*e*	0.4182(4)	0.2848(5)	0.1365(2)	0.029(3)	0.032(3)	0.049(3)	0.003(2)	0.008(3)	0.004(3)
N(3)	4*e*	0.1512(4)	0.4230(4)	0.1149(2)	0.024(2)	0.030(3)	0.020(2)	–0.002(2)	0.000(2)	–0.001(2)
N(4)	4*e*	–0.0872(3)	0.7361(4)	0.0885(2)	0.017(2)	0.028(3)	0.023(2)	–0.001(2)	0.003(2)	0.000(2)
N(5)	4*e*	–0.2016(4)	0.7837(4)	0.1476(2)	0.024(2)	0.035(3)	0.026(3)	0.006(2)	0.005(2)	0.000(2)
N(6)	4*e*	0.0479(4)	0.6134(4)	0.1852(2)	0.025(2)	0.032(3)	0.024(3)	0.001(2)	0.001(2)	0.003(2)
N(7)	4*e*	0.1720(4)	0.8591(5)	0.1873(2)	0.031(3)	0.040(3)	0.039(3)	–0.008(2)	0.006(3)	–0.007(3)
N(8)	4*e*	0.2983(6)	0.8435(6)	0.0473(3)	0.056(4)	0.048(4)	0.079(5)	0.002(3)	0.021(4)	0.030(4)
N(9)	4*e*	0.2133(4)	0.5515(5)	–0.0075(2)	0.033(3)	0.042(3)	0.032(3)	0.002(2)	0.007(3)	0.001(2)
O(1)	4*e*	0.3319(3)	0.5728(3)	0.1613(2)	0.025(2)	0.027(2)	0.033(2)	–0.002(2)	–0.003(2)	–0.000(2)
O(2)	4*e*	0.4054(4)	0.1723(4)	0.1278(3)	0.062(3)	0.040(3)	0.103(5)	0.009(3)	0.019(3)	0.002(3)
O(3)	4*e*	–0.0101(3)	0.6830(3)	0.0655(2)	0.022(2)	0.037(2)	0.028(2)	0.006(2)	0.007(2)	–0.001(2)
O(4)	4*e*	–0.2482(3)	0.7859(4)	0.1930(2)	0.041(3)	0.061(3)	0.037(3)	0.013(2)	0.017(2)	0.004(2)
O(5)	4*e*	0.2369(3)	0.7723(4)	0.1993(2)	0.037(2)	0.038(3)	0.043(3)	0.004(2)	–0.008(2)	–0.004(2)
O(6)	4*e*	0.1143(3)	0.8581(4)	0.1373(2)	0.040(3)	0.036(3)	0.047(3)	0.004(2)	–0.005(2)	–0.005(2)
O(7)	4*e*	0.1642(4)	0.9417(4)	0.2208(2)	0.057(3)	0.057(3)	0.057(3)	0.004(3)	0.002(3)	–0.034(3)
O(8)	4*e*	0.2036(4)	0.8084(4)	0.0252(2)	0.051(3)	0.050(3)	0.051(3)	0.007(2)	0.007(3)	0.020(2)
O(9)	4*e*	0.3353(4)	0.8008(4)	0.0964(2)	0.048(3)	0.044(3)	0.060(3)	–0.007(2)	0.000(3)	0.020(2)
O(10)	4*e*	0.3503(5)	0.9131(7)	0.0221(3)	0.091(5)	0.120(6)	0.142(7)	–0.025(4)	0.030(5)	0.088(5)
O(11)	4*e*	0.1203(3)	0.5715(4)	0.0057(2)	0.021(2)	0.061(3)	0.032(2)	0.009(2)	0.003(2)	–0.005(2)
O(12)	4*e*	0.2938(3)	0.5633(4)	0.0331(2)	0.023(2)	0.056(3)	0.034(2)	0.005(2)	0.000(2)	0.004(2)
O(13)	4*e*	0.2269(4)	0.5216(5)	–0.0568(2)	0.049(3)	0.082(4)	0.034(3)	0.005(3)	0.016(2)	–0.010(3)
C(1)	4*e*	0.5055(4)	0.4725(6)	0.1538(3)	0.017(3)	0.045(4)	0.043(4)	–0.001(3)	0.000(3)	0.008(3)
C(2)	4*e*	0.5207(5)	0.3493(6)	0.1254(3)	0.023(3)	0.049(4)	0.052(4)	0.001(3)	0.005(3)	0.008(4)
C(3)	4*e*	0.3383(4)	0.3656(5)	0.1432(2)	0.026(3)	0.029(3)	0.030(3)	0.001(2)	0.002(3)	0.007(2)
C(4)	4*e*	0.2214(4)	0.3366(5)	0.1388(2)	0.027(3)	0.027(3)	0.028(3)	–0.001(3)	0.004(2)	0.000(3)
C(5)	4*e*	0.1878(5)	0.2245(6)	0.1545(3)	0.043(4)	0.034(4)	0.046(4)	0.000(3)	–0.001(3)	0.011(3)
C(6)	4*e*	0.0773(6)	0.1979(7)	0.1441(3)	0.047(4)	0.044(4)	0.070(5)	–0.016(3)	0.007(4)	0.019(4)
C(7)	4*e*	0.0063(5)	0.2807(6)	0.1171(3)	0.029(3)	0.050(4)	0.065(5)	–0.017(3)	–0.002(4)	0.000(4)
C(8)	4*e*	0.0457(5)	0.3921(6)	0.1037(3)	0.022(3)	0.044(4)	0.038(4)	0.001(3)	–0.002(3)	–0.003(3)
C(9)	4*e*	0.5417(5)	0.5807(6)	0.1221(3)	0.034(4)	0.053(5)	0.064(5)	–0.011(3)	0.011(4)	0.014(4)
C(10)	4*e*	0.5500(5)	0.4784(7)	0.2181(3)	0.028(3)	0.088(6)	0.046(4)	–0.005(4)	–0.007(3)	0.006(4)
C(11)	4*e*	0.5138(6)	0.3533(7)	0.0596(3)	0.040(4)	0.073(5)	0.056(5)	–0.004(4)	0.018(4)	–0.002(4)
C(12)	4*e*	0.6218(5)	0.2777(7)	0.1512(4)	0.034(4)	0.062(5)	0.093(7)	0.021(4)	0.003(4)	0.012(5)
C(13)	4*e*	–0.1614(4)	0.8247(5)	0.0533(2)	0.027(3)	0.031(3)	0.024(3)	0.008(3)	0.004(2)	0.009(3)
C(14)	4*e*	–0.2274(5)	0.8751(5)	0.0999(3)	0.030(3)	0.029(3)	0.030(3)	0.003(3)	0.010(3)	0.001(3)
C(15)	4*e*	–0.1150(4)	0.7130(5)	0.1398(2)	0.017(3)	0.028(3)	0.028(3)	–0.002(2)	0.004(2)	–0.004(2)
C(16)	4*e*	–0.0623(4)	0.6256(5)	0.1821(2)	0.022(3)	0.029(3)	0.026(3)	–0.001(2)	0.005(2)	0.001(2)
C(17)	4*e*	–0.1228(5)	0.5612(6)	0.2166(3)	0.029(3)	0.053(4)	0.042(4)	0.000(3)	0.010(3)	0.014(3)
C(18)	4*e*	–0.0708(5)	0.4805(7)	0.2563(3)	0.045(4)	0.061(5)	0.043(4)	0.001(4)	0.017(3)	0.023(4)
C(19)	4*e*	0.0414(5)	0.4709(6)	0.2627(3)	0.051(4)	0.045(4)	0.040(4)	0.010(3)	0.004(3)	0.017(3)
C(20)	4*e*	0.0957(5)	0.5394(6)	0.2268(2)	0.032(3)	0.046(4)	0.027(3)	0.005(3)	0.002(3)	0.003(3)
C(21)	4*e*	–0.0913(6)	0.9156(6)	0.0273(3)	0.054(4)	0.046(4)	0.069(5)	0.010(4)	0.031(4)	0.027(4)
C(22)	4*e*	–0.2300(5)	0.7523(7)	0.0060(3)	0.049(4)	0.061(5)	0.038(4)	0.018(4)	–0.013(3)	–0.014(4)
C(23)	4*e*	–0.1833(6)	0.9957(6)	0.1264(3)	0.077(5)	0.038(4)	0.056(5)	–0.004(4)	0.018(4)	–0.013(4)
C(24)	4*e*	–0.3505(5)	0.8818(7)	0.0824(3)	0.029(3)	0.070(5)	0.047(4)	0.014(3)	0.009(3)	0.018(4)

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