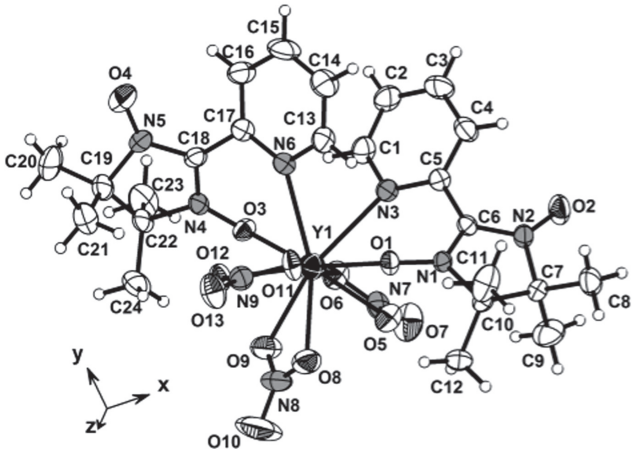
Dongjiao Li*

The crystal structure of tris(nitrato-κ²*O*,*O*′)-bis(4,4,5,5-tetramethyl-2-(*o*-pyridyl)imidazoline-1-oxyl 3-oxide-κ²*N*,*O*)yttrium(III), $C_{24}H_{32}N_9O_{13}Y$



https://doi.org/10.1515/ncrs-2020-0122
Received March 4, 2020; accepted April 8, 2020; available online April 29, 2020

Abstract

$C_{24}H_{32}N_9O_{13}Y$, monoclinic, $P2_1/n$ (no. 14), $a = 12.237(3)$ Å, $b = 11.058(3)$ Å, $c = 23.235(6)$ Å, $\beta = 98.486(4)°$, $V = 3109.6(14)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0455$, $wR_{ref}(F^2) = 0.0903$, $T = 293$ K.

CCDC no.: 1974362

The molecular complex title structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The ligand 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NIT2Py) was prepared following a slightly modified literature known procedure [6, 7]. $Y(NO_3)_3{\cdot}6\ H_2O$ (0.046 g, 0.2 mmol) and NIT2Py (0.047 g, 0.2 mmol) were dissolved in 10 mL 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 two week. Dark yellow crystals were obtained. **Elemental analysis** calcd. (%) for $C_{24}H_{32}N_9O_{13}$ Y: C, 38.77; H, 4.34; N, 16.96. Found (%): C, 38.70; H, 4.31; N, 16.90.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.24 × 0.20 × 0.18 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.96 mm^{-1}
Diffractometer, scan mode:	Bruker SMART APEXII, φ and ω
θ_{max}, completeness:	26.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	17527, 6348, 0.064
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4137
$N(param)_{refined}$:	432
Programs:	Bruker [1, 2], Olex2 [3], SHELX [4, 5]

Experimental details

The hydrogen atoms were generated geometrically using the riding model. The U_{iso} values of the hydrogen atoms of methyl groups were set to $1.5U_{eq}$(C) and the U_{iso} values of all other hydrogen atoms were set to $1.2U_{eq}$(C, N).

Comment

In the complex $[Y(III)(NIT2Py)_2(NO_3)_3]$, the metal ion is tenfold coordinated by two NIT2Py and three nitrate anions. The title structure is isomorphous to the structures of the directly related Eu(III) and Sm(III) complexes, respectively [8, 9]. The NIT2Py behaves as a bidentate chelating ligand *via* one oxygen of a nitronyl nitroxide and one nitrogen of a pyridyl group, however, the other oxygen of the nitronyl nitroxide keeps uncoordinated. The coordination sphere of the Y atom is completed by a κ²-coordination of three nitrate anions. The N(1)-O(1) and N(4)-O(3) (coordinated to Y(III) ion) bond lengths (1.289(3) Å and 1.299(3) Å) are longer than N(2)-O(2) and N(5)-O(4) to Y(III) ion) bond lengths (1.262(3) Å and 1.262(3) Å). The O(1)N(1)C(6)N(2)O(2) moiety is almost planar; minimum and maximum deviation of the atoms from this plane are 0.0132 Å for N(1) and 0.0016 Å for O(2), exhibiting the delocalization of π electrons. Dihedral angles between the pyridyl

***Corresponding author: Dongjiao Li,** School of Chemistry and Chemical Engineering, Linyi University, Linyi, China, e-mail: lidongjiao@lyu.edu.cn. https://orcid.org/0000-0001-5566-1365

Open Access. © 2020 Dongjiao Li, published by De Gruyter. This work is licensed under the Creative Commons Attribution 4.0 Public License.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Y1	0.82047(2)	0.83811(3)	0.89592(2)	0.02576(10)
O1	1.00813(17)	0.81739(19)	0.93399(9)	0.0289(5)
O2	1.24785(19)	0.7124(2)	0.80777(10)	0.0438(6)
O3	0.67111(17)	0.92402(19)	0.83854(9)	0.0300(5)
O4	0.5949(2)	1.3237(2)	0.87100(13)	0.0624(8)
O5	0.88601(18)	0.6457(2)	0.86379(10)	0.0395(6)
O6	0.76400(19)	0.7293(2)	0.80065(10)	0.0415(6)
O7	0.8365(2)	0.5590(2)	0.78054(12)	0.0595(8)
O8	0.8021(2)	0.6946(2)	0.97350(11)	0.0465(7)
O9	0.6685(2)	0.7010(2)	0.90245(12)	0.0477(7)
O10	0.6551(3)	0.5869(3)	0.97636(17)	0.1057(14)
O11	0.88104(17)	0.9286(2)	0.99191(10)	0.0373(6)
O12	0.70628(18)	0.9328(2)	0.96414(10)	0.0366(6)
O13	0.7718(2)	0.9776(2)	1.05412(11)	0.0504(7)
N1	1.0859(2)	0.7643(2)	0.91177(11)	0.0239(6)
N2	1.2015(2)	0.7154(2)	0.85278(11)	0.0284(6)
N3	0.9507(2)	0.8864(2)	0.81494(11)	0.0282(6)
N4	0.6201(2)	1.0226(2)	0.84938(11)	0.0268(6)
N5	0.5823(2)	1.2113(3)	0.86330(13)	0.0371(7)
N6	0.8517(2)	1.0733(2)	0.88504(11)	0.0274(6)
N7	0.8287(2)	0.6425(3)	0.81389(13)	0.0370(7)
N8	0.7067(3)	0.6584(3)	0.95152(16)	0.0533(9)
N9	0.7863(2)	0.9477(3)	1.00508(13)	0.0346(7)
C1	0.9014(3)	0.9596(3)	0.77310(14)	0.0358(9)
H1	0.824845	0.966013	0.768551	0.043*
C2	0.9564(3)	1.0258(3)	0.73649(15)	0.0443(10)
H2	0.918090	1.075985	0.708333	0.053*
C3	1.0694(3)	1.0162(4)	0.74243(17)	0.0503(11)
H3	1.109910	1.062917	0.719821	0.060*
C4	1.1211(3)	0.9359(3)	0.78257(15)	0.0413(9)
H4	1.197078	0.924244	0.785851	0.050*
C5	1.0611(3)	0.8733(3)	0.81764(13)	0.0263(8)
C6	1.1138(2)	0.7860(3)	0.86045(13)	0.0235(7)
C7	1.2266(3)	0.6241(3)	0.90099(14)	0.0285(8)
C8	1.3512(3)	0.6177(4)	0.91896(17)	0.0473(10)
H8A	1.385125	0.588495	0.886933	0.071*
H8B	1.367914	0.563665	0.951416	0.071*
H8C	1.379112	0.696823	0.929877	0.071*
C9	1.1830(3)	0.5035(3)	0.87523(17)	0.0552(11)
H9A	1.104959	0.509785	0.862336	0.083*
H9B	1.196637	0.441497	0.904327	0.083*
H9C	1.219879	0.483290	0.842807	0.083*
C10	1.1603(2)	0.6754(3)	0.94744(13)	0.0276(7)
C11	1.2292(3)	0.7486(4)	0.99487(16)	0.0525(11)
H11A	1.274857	0.804349	0.977552	0.079*
H11B	1.274987	0.695071	1.020545	0.079*
H11C	1.181137	0.792543	1.016503	0.079*
C12	1.0891(3)	0.5863(3)	0.97409(17)	0.0505(11)
H12A	1.049968	0.627561	1.001166	0.076*
H12B	1.134830	0.524388	0.994076	0.076*
H12C	1.037047	0.550327	0.943984	0.076*
C13	0.9575(3)	1.1046(3)	0.89631(15)	0.0339(8)
H13	1.007534	1.048096	0.914327	0.041*
C14	0.9974(3)	1.2158(4)	0.88289(18)	0.0495(11)
H14	1.072213	1.233496	0.891994	0.059*
C15	0.9257(3)	1.2994(4)	0.85612(18)	0.0514(11)
H15	0.951204	1.373824	0.845050	0.062*
C16	0.8146(3)	1.2717(3)	0.84567(15)	0.0395(9)
H16	0.763463	1.327878	0.828329	0.047*
C17	0.7812(3)	1.1595(3)	0.86145(13)	0.0285(7)
C18	0.6635(3)	1.1309(3)	0.85670(14)	0.0283(8)
C19	0.4799(3)	1.1471(3)	0.87374(15)	0.0383(9)
C20	0.3777(3)	1.2181(4)	0.8472(2)	0.0634(13)
H20A	0.379070	1.296859	0.864635	0.095*
H20B	0.312400	1.175802	0.854264	0.095*
H20C	0.377244	1.226117	0.806030	0.095*
C21	0.4857(3)	1.1424(4)	0.93970(16)	0.0518(11)
H21A	0.550102	1.097825	0.956235	0.078*
H21B	0.420811	1.103216	0.949371	0.078*
H21C	0.489895	1.223136	0.955028	0.078*
C22	0.4960(2)	1.0236(3)	0.84513(15)	0.0325(8)
C23	0.4514(3)	1.0174(4)	0.78074(16)	0.0536(11)
H23A	0.474749	1.087658	0.761547	0.080*
H23B	0.372097	1.014695	0.775646	0.080*
H23C	0.478947	0.946054	0.764268	0.080*
C24	0.4590(3)	0.9157(3)	0.87735(17)	0.0483(10)
H24A	0.473710	0.842761	0.857446	0.072*
H24B	0.381241	0.921804	0.878846	0.072*
H24C	0.498674	0.914154	0.916209	0.072*

substituents and the nitronyl nitroxide moieties are 36.1° and 34.3° for two NIT2Py in the compound, respectively. The Y-N(pyridyl) bond lengths are 2.646(3) Å and 2.692(3) Å. The Y-O(NO_3^-) bond lengths can be sorted out into two groups: (a) those with Y-O bond lengths (Y-O(5), Y-O(8), Y-O(9) and Y-O(11)) ranging from 2.421(2) Å to 2.457(2) Å and (b) those with bond lengths of 2.493(2) Å (Y-O(12)) and 2.525(2) Å (Y-O(6)). The bond lengths in the second group are longer, obviously. The nitronyl nitroxide groups are well spaced apart with the nearest O(2)–O(2), O(4)–O(4), and O(2)–O(4) extents being 6.148, 7.790, and 5.585 Å, respectively.

The Fourier Transform Infrared (FT-IR) spectrum of the title compound shows two characteristic strong bands in the 1500–1300 cm^{-1} region, which can be ascribed to the $\upsilon_{as}(NO_3^-)$ (1450 cm^{-1}) and $\upsilon_s(NO_3^-)$ (1300 cm^{-1}) vibrations of the coordinated nitrate groups. These two bands are divided 150 cm^{-1}, attributing to a bidentate coordination mode. Furthermore, the frequency of N—O stretch is 1360 cm^{-1} for free NIT2Py, and the frequency of N—O stretch is 1320 cm^{-1} for the compound. The red shift demonstrates the coordinated N—O group. The electronic spectrum of the compound in THF exhibits a strong, broad absorption centered around 606 nm ascribed to a n → π* transition [10, 11], and a peak around 367 nm can be ascribed to π → π* of the ONCNO group of the NIT2Py. The absorption around 260 nm can be ascribed to the π → π* transition of the 2-pyridyl group.

Acknowledgements: We acknowledge support from the National Natural Science Foundation of China (21505064).

References

1. Bruker. APEX3 and SAINT. Bruker AXS Inc., Madison, WI, USA (2016).
2. Bruker. SAINT, APEX2. Bruker AXS Inc., Madison, WI, USA (2009).
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Crystallogr. **42** (2009) 339–341.
4. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
5. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
6. Ullman, E. F.; Osiecki, J. H.; Boocock, D. G. B.; Darcy, R.: Stable free radicals. X. nitronyl nitroxide monoradicals and biradicals as possible small molecule spin labels. J. Am. Chem. Soc. **94** (1972) 7049–7059.
7. Ullman, E. F.; Call, L.; Osiecki, J. H.: Stable free radicals. VIII. new imino, amidino, and carbamoyl nitroxides. J. Org. Chem. **35** (1970) 3623–3631.
8. Li, D.-J.: 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-$\kappa^2 O,O'$)europium(III), $C_{24}H_{32}EuN_9O_{13}$. Z. Kristallogr. NCS **228** (2013) 197–198.
9. Li, D.-J.; Wang, S.-P.; Liao, D.-Z.; Jiang, Z.-H.; Yan, S.-P.: Synthesis, structures, magnetic and optical properties of two lanthanide [Ln = Sm(III), Dy(III)] complexes with chelating nitronyl nitroxide radicals. J. Mol. Struct. **698** (2004) 103–107.
10. Cabello, C. I.; Caneschi, A.; Carlin, R. L.; Gatteschi, D.; Rey, P.; Sessoli, R.: Structure and magnetic properties of ferromagnetic alternating spin chains. Inorg. Chem. **29** (1990) 2582–2587.
11. Li, D. J.; Gao, D. Z.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.: Synthesis, structure and magnetic properties of a Pr(III) complex with chelating nitronyl nitroxide radicals. J. Coord. Chem. **57** (2004) 1571–1576.