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The crystal structure of diaqua-tris(nitrato- κ^2O,O')-bis(4,4,5,5-tetramethyl-2-(*p*-pyridyl)imidazoline-1-oxyl 3-oxide- κN)samarium(III), $C_{24}H_{36}N_9O_{15}Sm$

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Abstract

$C_{24}H_{36}N_9O_{15}Sm$, monoclinic, $C2/c$ (no. 14), $a = 23.625(3)$ Å, $b = 11.6837(12)$ Å, $c = 11.9293(12)$ Å, $\beta = 94.6460(10)^\circ$, $V = 3281.9(6)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0173$, $wR_{ref}(F^2) = 0.0449$, $T = 293(2)$ K.

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The molecular 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-(4'-pyridyl)-4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NIT4Py) was prepared by a literature known procedure, which was slightly modified [6, 7]. $Sm(NO_3)_3 \cdot 6 H_2O$ (0.089 g, 0.2 mmol) and NIT4Py (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 brown crystals were obtained. **Elemental analysis** calcd. (%) for $C_{24}H_{36}N_9O_{15}$ Y: C, 34.28; H, 4.31; N, 14.99. Found (%): C, 35.11; H, 4.66; N, 16.01.

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Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.40 × 0.12 × 0.08 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.87 mm ⁻¹
Diffractometer, scan mode:	D8-APEX, φ and ω
θ_{max} , completeness:	25.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	8697, 2911, 0.019
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2726
$N(param)_{refined}$:	227
Programs:	Bruker [1, 2], Olex2 [3], SHELX [4, 5]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
Sm1	0.500000	0.11183(2)	−0.250000	0.02193(6)
O1	0.42666(6)	0.29059(15)	0.33533(12)	0.0372(4)
O2	0.27067(7)	0.37642(17)	0.09336(15)	0.0497(5)
O3	0.44811(6)	0.06877(15)	−0.43848(13)	0.0370(4)
O4	0.35777(7)	0.08084(17)	−0.48482(15)	0.0465(4)
O5	0.39203(7)	0.10947(18)	−0.31369(14)	0.0532(5)
O6	0.46159(7)	0.30488(15)	−0.30464(14)	0.0429(4)
O7	0.500000	0.4662(2)	−0.250000	0.0826(11)
O8	0.45809(8)	−0.05657(14)	−0.16981(13)	0.0439(4)
H8A	0.451706	−0.121116	−0.201208	0.066*
H8B	0.454446	−0.055216	−0.099508	0.066*
N1	0.44117(7)	0.18626(15)	−0.08151(13)	0.0253(4)
N2	0.37913(7)	0.33213(16)	0.29613(13)	0.0260(4)
N3	0.30360(7)	0.36687(16)	0.18237(15)	0.0291(4)
N4	0.39733(8)	0.08633(16)	−0.41408(15)	0.0301(4)
N5	0.500000	0.3625(3)	−0.250000	0.0457(8)
C1	0.44179(9)	0.29381(19)	0.08986(17)	0.0287(5)
H1	0.462229	0.337403	0.144398	0.034*
C2	0.46778(9)	0.25043(19)	−0.00029(17)	0.0278(5)
H2	0.506051	0.266619	−0.005107	0.033*
C3	0.38603(9)	0.16465(19)	−0.07163(17)	0.0272(4)
H3	0.366760	0.119524	−0.126465	0.033*
C4	0.35621(9)	0.20499(19)	0.01443(17)	0.0272(5)
H4	0.317834	0.188251	0.016778	0.033*
C5	0.38459(8)	0.27135(18)	0.09791(16)	0.0245(4)
C6	0.35593(8)	0.32050(18)	0.19031(16)	0.0248(4)
C7	0.28613(9)	0.40062(18)	0.29669(19)	0.0282(5)
C8	0.25152(11)	0.3015(2)	0.3369(2)	0.0468(6)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H8C	0.220419	0.285833	0.282170	0.070*
H8D	0.237056	0.321141	0.407295	0.070*
H8E	0.275190	0.234895	0.346567	0.070*
C9	0.25084(11)	0.5090(2)	0.2879(2)	0.0469(6)
H9A	0.270797	0.566937	0.249823	0.070*
H9B	0.244212	0.535269	0.361978	0.070*
H9C	0.215145	0.493506	0.246389	0.070*
C10	0.34519(9)	0.41341(19)	0.36217(18)	0.0284(5)
C11	0.34812(13)	0.3784(2)	0.4848(2)	0.0498(7)
H11A	0.339408	0.298401	0.490112	0.075*
H11B	0.321142	0.422158	0.522932	0.075*
H11C	0.385657	0.392381	0.519059	0.075*
C12	0.37175(11)	0.5307(2)	0.3491(2)	0.0472(6)
H12A	0.410185	0.529808	0.382086	0.071*
H12B	0.350363	0.586986	0.386287	0.071*
H12C	0.371477	0.549214	0.270661	0.071*

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 1.5*U*_{eq}(C) and the *U*_{iso} values of all other hydrogen atoms were set to 1.2*U*_{eq}(C, N).

Comment

In the complex [Sm(III)(NIT4Py)₂(NO₃)₃(H₂O)₂], the Sm(III) ion is located slightly twisted in a tenfold coordinated dicapped square anti-prism center, in which the oxygen atom O5 and O5A from nitrate anion act as cap, N1, O3, O6, O8, N1A, O3A, O6A and O8A from two NIT4Py, two aqua ligands and chelating nitrate anions comprise a distorted square anti-prism. The water molecules occupy adjacent positions in the complex. The coordinated Sm–N bond (2.6797(2) Å) is longer than the coordinated Sm–O bond lengths (2.4331(2)–2.6021(3) Å). Only one nitrogen atom of pyridine is coordinated and the oxygen atoms are uncoordinated [8, 9]. A hydrogen bond is formed between the coordinated water molecules O8 and O3 in a nitrate anion. One further hydrogen bond is found between the water ligand O8 and nitronyl nitroxide O1. The FT-IR spectrum of the title compound exhibits two characteristic strong bands in the 1510–1300 cm^{−1} region, which can be ascribed to the *ν*_{as}(NO₃[−]) (1450 cm^{−1}) and *ν*_a(NO₃[−]) (1305 cm^{−1}) modes of the coordinated NO₃[−]. These two peaks are divided by 145 cm^{−1}, attributing to a bidentate coordination mode. The asymmetric stretching vibration band is

near 1460 cm^{−1} and the symmetric stretching vibration band is near 1310 cm^{−1}. The band of the N–O in NIT4Py can be clearly observed at 1371 cm^{−1}, which indicates that N–O is uncoordinated [10, 11]. The band at 3360 cm^{−1} is attributed to the O–H stretching vibration of the coordinated water molecules. All parameters are similar to the isomorphous praseodym(III) structure [12].

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