

氮氧自由基单核钬配合物的合成与结构

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Synthesis and Crystal Structure of a Mononuclear Ho(III) Nitronyl Nitroxide Radical Complex

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Abstract: A novel mononuclear Ho(III) nitronyl nitroxide complex [Ho(hfac)₃(NITPhDma)₂], (NITPhDma=2-(4-dimethylamino-phenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, hfac=hexafluoroacetylacetonate), was synthesized and structurally characterized by X-ray diffraction. It crystallizes in monoclinic, space group $P2_1/n$ with $a=1.274\ 5(1)$ nm, $b=1.753\ 1(2)$ nm, $c=2.482\ 8(2)$ nm, $\beta=93.753(2)^\circ$. The Ho(III) ion is eight-coordinated with a distorted dodecahedron environment. Each NITPhDma radical acts as monodentate ligand towards Ho(III) ion through the NO group, and the complex molecules are well isolated. CCDC: 775839.

Key words: nitronyl nitroxide radical; holmium(III) complex; crystal structure

In recent years the fascinating magnetic behaviors of single-molecule magnets (SMMs) and single-chain magnets (SCMs), such as the slow relaxation of magnetisation, magnetic hysteresis and the quantum tunnelling (QT) of magnetisation, have aroused deep interest from both applicative and theoretical points of view^[1-2]. They have been proposed as candidates for high-density information storage and quantum computation^[3]. These magnetic properties is the result of the combination of a large ground state spin value, a significant uniaxial

(Ising) magnetic anisotropy, inter- and intra- molecular magnetic coupling, etc. As well known, lanthanide ions, especially heavy lanthanide ions, show a large magnetic anisotropy based on their large spin-orbit coupling. So they have become the best candidates for the construction of SMMs and SCMs in the field of molecular engineering^[4-6].

Radicals of the nitronyl nitroxide family (NITR) also attract much attention since the discovery of the first SCM by Gatteschi^[7]. Since then, much work has

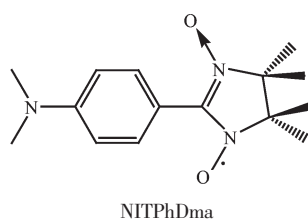
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been reported on the lanthanide-radical complexes in the pursuit of SMMs and SCMs^[8-14]. The different R substituents on NITR can influence the steric structure dimensionality of complex, the coordination mode of NITR, the inter- and intra-molecular magnetic interaction. So the introducing of NITR ligands is one of the most elegant ways to tune the magnetic properties of complexes. Herein, we report a mononuclear lanthanide-radical complex $[\text{Ho}(\text{hfac})_3(\text{NITPhDma})_2]$ (hfac=hexafluoroacetylacetonate) based on a new nitronyl nitroxide radical NITPhDma.



1 Experimental

1.1 Synthesis of $[\text{Ho}(\text{hfac})_3(\text{NITPhDma})_2]$

All reagents were of A.R. grade and used as received. 2-(4'-dimethylamino-phenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NITPhDma) was prepared according to the methods reported^[15]. $\text{Ho}(\text{hfac})_3 \cdot 2\text{H}_2\text{O}$ was prepared according to the literature^[10].

A solution of 1 mmol of $\text{Ho}(\text{hfac})_3 \cdot 2\text{H}_2\text{O}$ in 30 mL of dry n-heptane was heated under reflux for 30 min, and then cooled to 70 °C. After that, a solution of 1 mmol of solid NITPhDma in 3 mL of CH_2Cl_2 was added

under stirring. The resulting mixture was refluxed for 30 min and then cooled to room temperature. After filtration, the filtrate was left at 5 °C. Deep blue-green single crystals suitable for X-ray structure analysis were obtained by the slow evaporation of filtrate for about one week. IR spectrum: ν/cm^{-1} , 1 655(s), 1 610(m), 1 375(w), 1 350(vw), 1 256(m), 1 196(s), 1 142(vs), 793(m), 662(s), 617(m).

1.2 Crystal structure determination

A deep blue-green crystal of the title complex with approximate dimensions of 0.21 mm × 0.16 mm × 0.06 mm was put on a Bruker SMART APEX II CCD area detector, equipped with a graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). Data were collected at room temperature by φ - ω scan mode. The structure was solved with direct methods using SHELXS-97 program^[16]. The H atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full matrix least-squares refinement on F^2 was carried out using SHELXL-97^[17]. Reliability factors were defined as $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$, and the function minimized was $wR_2 = (\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2)^{1/2}$, where in the least squares calculation the unit weight was used. All nonhydrogen atoms were refined anisotropically. Crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond distances and angles are listed in Table 2.

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Table 1 Crystal data and structure refinement for title complex

Formula	$\text{C}_{45}\text{H}_{47}\text{F}_{18}\text{HoN}_6\text{O}_{10}$	$F(000)$	2672
Formula weight	1 338.82	θ rang for data collection / (°)	1.42 to 25.05
Temperature / K	273(2)	Limiting indices	$-15 \leq h \leq 14, -10 \leq k \leq 20, -29 \leq l \leq 29$
Wavelength / nm	0.071 073	Reflections collected / unique (R_{int})	28 553 / 9 793 (0.043 1)
Crystal system	Monoclinic	Observed reflections ($I > 2\sigma(I)$)	6 593
Space group	$P2_1/n$	Refinement method	Full-matrix least-squares techniques on F^2
a / nm	1.274 5(1)	Data / restraints / parameters	9 793 / 252 / 805
b / nm	1.753 1(2)	Goodness-of-fit on F^2	1.014
c / nm	2.482 8(2)	Final R indices ($I > 2\sigma(I)$)	$R_1=0.037\ 2, wR_2=0.078\ 5$
β / (°)	93.753(2)	R indices (all data)	$R_1=0.070\ 4, wR_2=0.091\ 9$
Volume / nm ³	5.535 4(9)	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	470 and -459
Z	4	Weighting scheme ($P=(F_o^2+2F_c^2)/3$)	$w=1/[\sigma^2(F_o^2)+(0.041\ 3P)^2+1.125\ 6P]$
Calculated density / ($\text{g} \cdot \text{cm}^{-3}$)	1.606	$(\Delta/\sigma)_{\text{max}}$	0.116
Absorption coefficient / mm^{-1}	1.548		

Table 2 Selected bond lengths (nm) and bond angles (°)

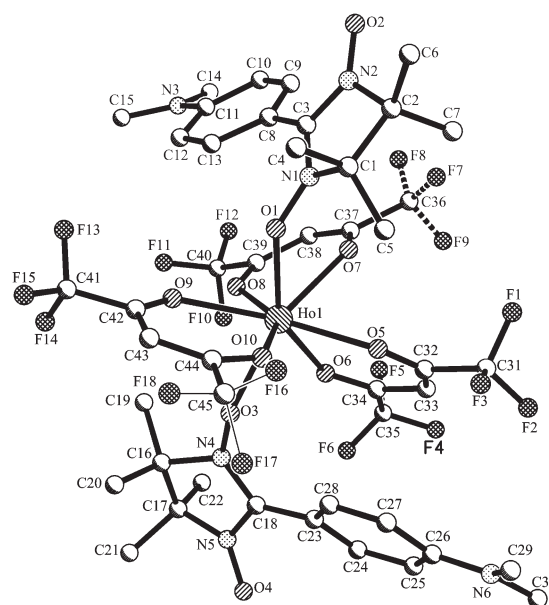
Ho(1)-O(1)	0.231 3(3)	Ho(1)-O(3)	0.228 3(3)	Ho(1)-O(5)	0.231 0(3)
Ho(1)-O(6)	0.239 4(4)	Ho(1)-O(7)	0.237 9(3)	Ho(1)-O(8)	0.230 2(3)
Ho(1)-O(9)	0.235 8(3)	Ho(1)-O(10)	0.236 8(3)	O(1)-N(1)	0.129 7(4)
O(2)-N(2)	0.126 3(5)	O(3)-N(4)	0.131 0(5)	O(4)-N(5)	0.127 9(6)
O(5)-C(32)	0.124 9(6)	O(6)-C(34)	0.122 9(6)	O(7)-C(37)	0.123 8(6)
O(8)-C(39)	0.123 6(6)	O(9)-C(42)	0.123 4(5)	O(10)-C(44)	0.123 6(5)
O(3)-Ho(1)-O(7)	148.10(13)	O(3)-Ho(1)-O(9)	74.88(11)	O(3)-Ho(1)-O(6)	73.68(12)
O(3)-Ho(1)-O(5)	100.87(12)	O(3)-Ho(1)-O(1)	137.54(12)	O(3)-Ho(1)-O(8)	93.16(12)
O(3)-Ho(1)-O(10)	71.47(11)	O(7)-Ho(1)-O(9)	125.98(11)	O(7)-Ho(1)-O(6)	74.76(12)
O(7)-Ho(1)-O(5)	73.83(12)	O(7)-Ho(1)-O(1)	74.30(12)	O(7)-Ho(1)-O(8)	73.23(12)
O(7)-Ho(1)-O(10)	133.55(11)	O(9)-Ho(1)-O(6)	132.84(12)	O(9)-Ho(1)-O(5)	147.91(12)
O(9)-Ho(1)-O(1)	72.16(10)	O(9)-Ho(1)-O(8)	74.61(11)	O(9)-Ho(1)-O(10)	73.54(11)
O(6)-Ho(1)-O(5)	72.79(12)	O(6)-Ho(1)-O(1)	148.57(11)	O(6)-Ho(1)-O(8)	73.01(12)
O(6)-Ho(1)-O(10)	126.13(12)	O(5)-Ho(1)-O(1)	93.30(12)	O(5)-Ho(1)-O(8)	137.37(12)
O(5)-Ho(1)-O(10)	74.99(12)	O(1)-Ho(1)-O(8)	102.99(11)	O(1)-Ho(1)-O(10)	74.04(11)
O(8)-Ho(1)-O(10)	147.28(11)				

2 Results and discussion

The IR spectrum of the title complex was compared with that of the radical ligand. The characteristic absorption of the O-N stretching vibration at $1\,387\text{ cm}^{-1}$ for NITPhDma is shifted to lower frequencies at $1\,375\text{ cm}^{-1}$ for the complex, indicating that the NO groups are bonded to the central ion, which was confirmed by X-ray diffraction analysis.

The X-ray analysis showed that the title complex crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit consists of a discrete mononuclear molecule (Fig.1). The central Ho(III) ion located in a distorted dodecahedron environment with triangular faces, in which the eight coordination sites are occupied by six oxygen atoms from three hfac ligands, two oxygen atoms from two NITPhDma radicals. The NITPhDma radical acts as monodentate ligand towards Ho(III) ion through the NO group, so the bond lengths of coordinated groups O1-N1 and O3-N4 (0.129 7(4) and 0.131 0(5) nm) are longer than the bond lengths of uncoordinated NO groups O2-N2 and O4-N5 (0.126 3(5) and 0.127 9(6) nm). It is noted that some fluorine atoms of hfac ligands are disorder, especially F7, F8 and F9 and F16, F17 and F18 (Fig.1). The shortest intermolecular Ho(III) \cdots Ho(III) separation is

1.078 7 nm, implying the complex molecules are well isolated. The nearest intermolecular N-O \cdots O-N contact of the nitroxide groups is 0.292 1 nm, which exists among some uncoordinated O4 atoms.



All hydrogen atoms are omitted for clarity

Fig.1 ORTEP drawing of complex $[\text{Ho}(\text{hfac})_3(\text{NITPhDma})_2]$ with the atom-labeling and 50% thermal ellipsoids

The thermal decomposition curves of the complex $[\text{Ho}(\text{hfac})_3(\text{NITPhDma})_2]$ showed that the complex begin to decompose at $50\text{ }^\circ\text{C}$ and end at $750\text{ }^\circ\text{C}$. The removal

of principal organic ligands took place in the range of 155~412 °C. The complex was completely degraded into Ho_2O_3 with a total loss of 85.68% (theoretical loss is 85.89%).

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