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联吡啶四氮唑单核钆(Ⅲ)配合物的甲基化影响

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摘要：应用 6-(氢-5-四氮唑基)-2,2′-联吡啶(tbpyH)和 6-(氢-5-四氮唑基)-4,4′-二甲基-2,2′-联吡啶(tmbpyH)配体,合成得到 2 个新的单核钆(Ⅲ)配合物[Gd(tbpy)$_2$(DMF)(H$_2$O)$_2$]NO$_3$·2H$_2$O (**1**)和[Gd(tmbpy)$_2$(DMF)(NO$_3$)]·DMF·THF (**2**)。X 射线单晶衍射表明,每个钆(Ⅲ)离子均表现为 1 个畸变的三冠三角棱柱体，包含了 2 个四氮唑基 N-H 去质子化而产生的一价阴离子三齿螯合配体。此外,在 2,2′-联吡啶环上引入 2 个甲基对钆(Ⅲ)金属中心的配位环境有显著影响,表现为 2 个单齿配位的水分子被 1 个螯合配位的硝酸根离子取代。

关键词：钆(Ⅲ)配合物；联吡啶四氮唑；甲基化；晶体结构
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Effect of the Methylation on Mononuclear Gd(Ⅲ) Bipyridyl Tetrazolate Complexes

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Abstract: Two new mononuclear Gd(Ⅲ) complexes, [Gd(tbpy)$_2$(DMF)(H$_2$O)$_2$]NO$_3$·2H$_2$O (**1**) and [Gd(tmbpy)$_2$(DMF)(NO$_3$)]·DMF·THF (**2**), have been synthesized by using 6-(1*H*-tetrazole-5-yl)-2,2′- bipyridyle (tbpyH) and 6-(1*H*-tetrazole-5-yl)-4,4′-dimethyl-2,2′-bipyridyle (tmbpyH). As revealed by single-crystal X-ray diffraction, each Gd(Ⅲ) ion has a distorted tricapped trigonal prism with two mono-anionic tridentate chelating ligands, originating from N-H deprotonation of the tetrazolyl ring, and the introduction of two methyl groups into the 2,2′-bypridyl ring has a significant effect on the coordination environment of the Gd(Ⅲ) core, showing that two mono-coordinated H$_2$O molecules are displaced by one chelating nitrate. CCDC: 1496645, **1**; 1496646, **2**.

Keywords: Gd(Ⅲ) complex; bipyridyl tetrazole; methylation; crystal structure

0 Introduction

Lanthanide(Ⅲ) complexes have sparked a rapidly growing interest owing to their widely potential applications in many fields such as lighting, display, analytical sensor, and biomedical imaging[1-7]. Recently, synthesis of Ln (Ⅲ) coordination compounds with polydentate N-donor and/or N,O-donor ligands has attracted much attention[8-21]. It is reported that anionic polydentate ligands with deprotonated arylamide[9-10], triazole[11-13] or tetrazole[14-22] moieties can give the moisture- and air-stable Ln(Ⅲ) complexes with the Ln-

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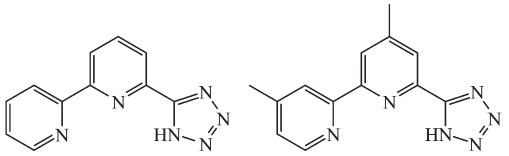
N bonds, because of their good binding abilities to the lanthanide ions.

Mono-anionic polydentate chelating ligand is a preferred candidate, which can saturate the coordination sphere of the Ln(Ⅲ) ion and completely compensate the charge in the case where tris-ligand complexes are generated, an advantage for application in photoelectric devices. Bipyridyl tetrazole (Scheme 1) may be an alternative class of N-heterocyclic ligands which may be easily modified and generate strong bonding with transition metals, giving robust complexes, where the N-H deprotonation of the tetrazolyl ring gives rise to the mono-anionic tridentate chelating ligands[23-26]. Herein, we report the synthesis and crystal structures of two new mononuclear Gd (Ⅲ) complexes with deprotonated bipyridyl tetrazole tridentate chelating ligands, and the influence of the methylation of the 2,2′ -bipyridyl ring on the structures of Gd (Ⅲ) complexes.



Scheme 1 Structures of the tbpyH and tmbpyH ligands

1 Experimental

1.1 Materials and measurements

All the chemicals used for synthesis were of analytical grade and used without further purification unless otherwise stated. 6-(1*H*-tetrazole-5-yl)-2,2′-bipyridyle (tbpyH) and 6-(1*H*-tetrazole-5-yl)-4,4′-dimethyl-2,2′-bipyridyle (tmbpyH) were synthesized according to literature methods[23-24]. Elemental analyses of carbon, hydrogen and nitrogen were conducted on a Perkin-Elmer model 240C elemental analyzer. Infrared (IR) spectra were recorded on a Bruker Optics ALPHA FT-IR spectrometer using KBr pellets. Crystal structures were determined on a Bruker D8 QUEST diffractometer.

1.2 Preparations of complexes 1 and 2

1.2.1 $[Gd(tbpy)_2(DMF)(H_2O)_2]NO_3\cdot 2H_2O$ (**1**)

An ethanol solution (10 mL) of $Gd(NO_3)_3\cdot 6H_2O$ (32.1 mg, 0.071 mmol) and tbpyH (49.3 mg, 0.220 mmol) was refluxed for 12 h, giving a white precipitate. The precipitate was isolated by filtration, washed with diethyl ether and dried under vacuum. Colorless crystals of **1** were afforded via slow diffusion of CH_3CN into the DMF solution of **1** after 6 days. Yield: 46% (based on $Gd(NO_3)_3\cdot 6H_2O$). Anal. Calcd. for $C_{25}H_{29}GdN_{14}O_8$(%): C, 37.03; H, 3.60; N, 24.18. Found(%): C, 37.06; H, 3.63; N, 24.14. IR (KBr, cm^{-1}): 3 412(m), 3 083(w), 1 663(vs, C=O), 1 601(s), 1 429(vs), 1 384(vs, NO_3^-), 1 314(m), 1 243(w), 1 186(w), 1 110(w), 1 060(w), 1 009(m), 829(w), 790(m), 758(m), 688(m).

1.2.2 $[Gd(tmbpy)_2(DMF)(NO_3)]\cdot DMF\cdot THF$ (**2**)

Complex **2** was synthesized following the procedure for **1**, using $Gd(NO_3)_3\cdot 6H_2O$ (52.2 mg, 0.116 mmol) and tmbpyH (90.4 mg, 0.358 mmol). Colorless crystals of **2** were afforded by slow diffusion of THF into the DMF solution of **2** after 5 days. Yield: 41% (based on $Gd(NO_3)_3\cdot 6H_2O$). Anal. Calcd. for $C_{36}H_{44}GdN_{15}O_6$(%): C, 45.99; H, 4.72; N, 22.35. Found(%): C, 45.94; H, 4.75; N, 22.32. IR (KBr, cm^{-1}): 3 431 (m), 3 066(w), 2 926(w), 2 588(w), 1 656(s, C=O), 1 618(vs), 1 564(m), 1 482(m), 1 388(s, NO_3^-), 1 239(vs), 1 157(vs), 1 010(m), 940(m), 877(w), 835(w), 789(w), 748(w), 687(w), 628(m), 553(m), 505(s), 432(w).

1.3 X-ray crystallography

The measurements of single crystals of **1** and **2** were performed on a Bruker D8 QUEST diffractometer using a graphite-monochromated Mo $K\alpha$ radiation (λ= 0.071 073 nm). The program CrystalClear was used for the integration of the diffraction profile. Structures were solved by direct methods and refined by full-matrix least-squares technique on F^2 using the SHELXTL software package[27-28]. The heavy atoms were located from *E*-map and other non-hydrogen atoms were found in subsequent difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were generated geometrically with isotropic thermal parameters. The crystallographic data and structure refinement details of **1** and **2** are listed in Table 1, and the selected bond lengths and angles for **1** and **2** are summarized in Table 2.

CCDC: 1496645, **1**; 1496646, **2**.

Table 1　Crystal data and structure refinement for 1 and 2

Complex	**1**	**2**
Empirical formula	$C_{25}H_{29}GdN_{14}O_8$	$C_{36}H_{44}GdN_{15}O_6$
Formula weight	810.87	940.11
Crystal system	Monoclinic	Triclinic
Space group	$P2/c$	$P\bar{1}$
a / nm	1.143 39(7)	0.953 22(6)
b / nm	1.161 83(7)	1.309 49(8)
c / nm	1.449 92(7)	1.788 14(11)
α / (°)	90	100.969(2)
β / (°)	123.205(3)	96.977(2)
γ / (°)	90	108.096(2)
V / nm^3	1.611 61(16)	2.043 5(2)
Z	2	2
D_c / (g·cm^{-3})	1.671	1.528
Absorption coefficient / mm^{-1}	2.127	1.686
θ range / (°)	3.33~26.77	3.18~26.81
F(000)	810	954
Reflections collected, unique	25 869, 3 447	32 919, 8 594
Data, restraints, parameters	3 447, 61, 254	8 594, 9, 523
R_{int}	0.041 3	0.045 1
Goodness-of-fit (GOF) on F^2	1.088	1.086
R_1, wR_2 [$I>2\sigma(I)$]	0.034 4, 0.086 3	0.054 1, 0.111 4
R_1, wR_2 (all data)	0.041 6, 0.092 4	0.073 8, 0.120 9
Largest difference peak and hole / (e·nm^{-3})	719 and −786	1 805 and −807

Table 2　Selected bond lengths (nm) and angles (°) for 1 and 2

Complex **1**					
Gd1-O1	0.242 1(3)	Gd1-O2	0.241 2(5)	Gd1-N1	0.258 5(4)
Gd1-N2	0.259 9(3)	Gd1-N3	0.249 8(3)		
O1-Gd1-O2	69.57(8)	O1-Gd1-O1^{i}	139.14(16)	O1-Gd1-N1	81.43(12)
O1-Gd1-N2	134.80(11)	O1-Gd1-N3	138.26(11)	O1-Gd1-N1^{i}	88.54(12)
O1-Gd1-N2i	69.45(10)	O1-Gd1-N3^{i}	78.13(11)	O2-Gd1-N1	75.52(10)
O2-Gd1-N2	120.42(7)	O2-Gd1-N3	140.73(8)	N1-Gd1-N2	62.16(12)
N1-Gd1-N3	126.30(12)	N1-Gd1-N1^{i}	151.0(2)	N1-Gd1-N2^{i}	136.07(12)
N1-Gd1-N3^{i}	78.18(12)	N2-Gd1-N3	64.45(11)	N2-Gd1-N1^{i}	136.07(12)
N2-Gd1-N2^{i}	119.16(15)	N2-Gd1-N3^{i}	69.35(10)	N3-Gd1-N1^{i}	78.18(12)
N3-Gd1-N2^{i}	69.35(10)	N3-Gd1-N3^{i}	78.54(16)		
Complex **2**					
Gd1-O1	0.235 0(4)	Gd1-O2	0.250 0(4)	Gd1-O4	0.252 0(4)
Gd1-N1	0.255 7(4)	Gd1-N2	0.254 6(4)	Gd1-N3	0.247 8(5)
Gd1-N7	0.254 6(4)	Gd1-N8	0.255 3(4)	Gd1-N9	0.248 6(5)
O1-Gd1-O2	123.17(16)	O1-Gd1-O4	72.76(15)	O1-Gd1-N1	80.74(14)
O1-Gd1-N2	72.03(14)	O1-Gd1-N3	80.92(15)	O1-Gd1-N7	86.18(14)
O1-Gd1-N8	143.91(14)	O1-Gd1-N9	144.81(15)	O2-Gd1-O4	50.42(15)

Continued Table 2

O2-Gd1-N1	86.34(15)	O2-Gd1-N2	144.99(15)	O2-Gd1-N3	142.27(15)
O2-Gd1-N7	77.81(15)	O2-Gd1-N8	70.93(14)	O2-Gd1-N9	78.98(16)
O4-Gd1-N1	78.41(14)	O4-Gd1-N2	131.42(14)	O4-Gd1-N3	138.27(15)
O4-Gd1-N7	71.21(15)	O4-Gd1-N8	111.06(14)	O4-Gd1-N9	122.97(16)
N1-Gd1-N2	63.81(14)	N1-Gd1-N3	128.92(15)	N1-Gd1-N7	149.32(15)
N1-Gd1-N8	135.29(14)	N1-Gd1-N9	73.33(15)	N2-Gd1-N3	65.23(14)
N2-Gd1-N7	137.09(14)	N2-Gd1-N8	117.17(14)	N2-Gd1-N9	75.31(14)
N3-Gd1-N7	75.32(15)	N3-Gd1-N8	73.48(14)	N3-Gd1-N9	97.11(16)
N7-Gd1-N8	63.19(14)	N7-Gd1-N9	127.63(15)	N8-Gd1-N9	64.99(14)

Symmetry codes: ^{i} $-x$, y, $0.5+z$

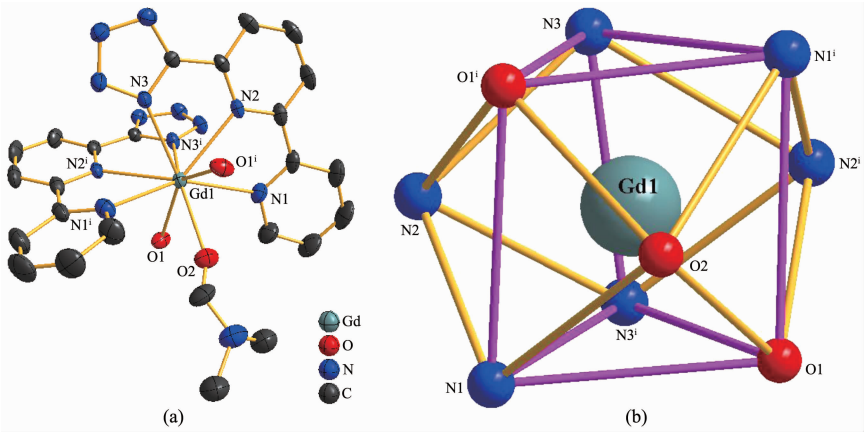
2 Results and discussion

2.1 Synthesis and characterization

Mononuclear Gd(Ⅲ) complexes **1** and **2**, instead of the expected tris-ligand species [Gd(L)$_3$], were successfully obtained by refluxing $Gd(NO_3)_3\cdot 6H_2O$ with three equivalents of bipyridyl tetrazole (tbpyH or tmbpyH) ligands in ethanol solution, followed by crystallization from CH_3CN or THF into the DMF solution of relative complex. This suggests that the Gd(Ⅲ) cation only can coordinate with two equivalents of bipyridyl tetrazole chelating ligands in refluxing ethanol, and the resulting Gd(Ⅲ) complexes with two bipyridyl tetrazolate ligands may be more thermodynamically stable relative to tris-ligand species. In IR spectra, a strong absorption peak is observed at 1 384 and 1 388 cm^{-1} for **1** and **2**, respectively, which is from the stretching vibration of the NO_3^- anion [29]. Moreover, another strong absorption peak is also observed at 1 663 and 1 656 cm^{-1} for **1** and **2**, respectively, attributable to the carbonyl stretching vibration ($\nu_{C=O}$) of the coordinated DMF solvent molecule[26,30].

2.1 Crystal structural description

The exact structures of **1** and **2** were established by single-crystal X-ray crystallography. Complex **1** crystallizes in the monoclinic system, space group *P*2/*c*. The asymmetric unit of **1** contains one [Gd(tbpy)(DMF)$(H_2O)_2$]$^+$ cation, one NO_3^- anion and two H_2O solvent molecules. As indicated in Fig.1a, the Gd(Ⅲ) ion of **1** is nine-coordinated by six N atoms from two mono-anionic tbpy tridentate chelates and three O atoms from one DMF and two H_2O molecules. The coordination polyhedron around the Gd(Ⅲ) center can be described as a distorted tricapped trigonal prism (Fig.1b), with two N atoms from the central pyridyl rings of two tmbpy chelates and one O atom from one



Symmetry codes: ^{i} $1-x$, y, $0.5-z$

Fig.1 Molecular structure of the cation with 30% probability ellipsoids (a) and coordination geometry around the Gd(Ⅲ) ion (b) of complex **1**

DMF molecule in capping positions (these three atoms [N, N and O] are in-plane with the Gd(Ⅲ) cation). The tbpy ligand ligates the Gd(Ⅲ) ion in a mono-anionic tridentate chelating coordination fashion via the N-H cleavage of the tetrazolyl ring. The Gd1-N3 distance (0.249 8(3) nm) (tetrazolyl-N atom) is shorter than those between the Gd(Ⅲ) ion and the pyridyl-N atoms (Gd1-N1 0.258 5(4) nm; Gd1-N2 0.259 9(3) nm], implying a stronger bonding of the Gd(Ⅲ) ion to the tetrazolyl-N atom and a significant influence of the N-H deprotonation of the tetrazolyl ring on the binding strength of the ligand. The Gd1-O1 distance (hydrate oxygen atom) is 0.242 1(3) nm, and the Gd1-O2 length (DMF oxygen atom) is 0.241 2(5) nm.

However, complex **2** crystallizes in the triclinic system, space group $P\bar{1}$, in which tmbpy exhibits a mono-anionic tridentate chelating coordination manner similar to the tbpy ligand of **1**. The asymmetric unit of **2** includes one [Gd(tmbpy)(DMF)(NO_3)] molecule, one DMF and one THF solvent molecule. As shown in Fig.2a, the coordination number of the Gd(Ⅲ) ion is also nine, similar to **1**, of which seven positions are also occupied by six N atoms from two mono-anionic tmbpy tridentate chelating ligands and one O atom from one DMF solvent molecule, the remaining two positions are occupied by two O atoms from one chelating nitrate anion instead of two coordinated H_2O molecules of **1**. Analogous to **1**, the coordination geometry around the Gd(Ⅲ) ion of **2** is also a distorted tricapped trigonal prism (Fig.2b), with two N atom from the central pyridyl rings of two tmbpy chelates and one O atom from the nitrate anion in capping positions (these three atoms [N, N and O] are also in-plane with the Gd(Ⅲ) ion). The Gd-$N_{tetrazolyl}$ distances (Gd1-N3 0.247 8(5) nm; Gd1-N9 0.248 6(5) nm) are shorter than the Gd-$N_{pyridyl}$ lengths (Gd1-$N_{pyridyl}$ 0.254 6(4) ~0.255 7(4) nm), indicative of a stronger bonding of the Gd(Ⅲ) ion to the tetrazolyl-N atom. It is also noted that the Gd-N lengths of **2** are slightly shorter than those of **1**, implying an important influence of two electron-donating methyl groups on the bipyridyl tetrazole chelate. As is further supported by the fact that the Gd1-O1 length (DMF oxygen atom) of **2** (0.235 0(4) nm) is somewhat shorter than the Gd1-O2 length (DMF oxygen atom) of **1** (0.241 2(5) nm). The Gd-$O_{nitrate}$ distances are 0.250 0(4) and 0.252 0(4) nm.

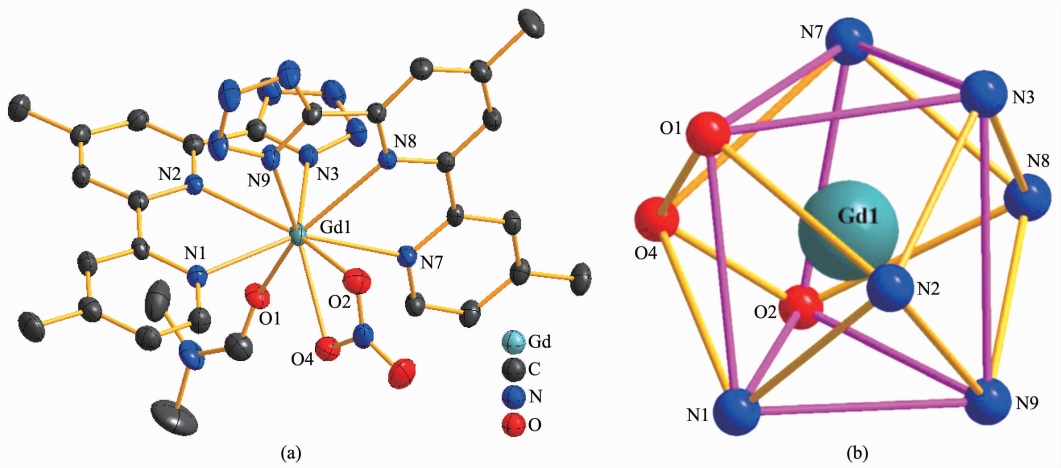


Fig.2　Molecular structure of the cation with 30% probability ellipsoids (a) and coordination geometry around the Gd(Ⅲ) ion (b) of complex **2**

3　Conclusions

We have synthesized and characterized two new mononuclear Gd(Ⅲ) complexes with deprotonated bipyridyl tetrazole tridentate chelating ligands, $[Gd(tbpy)_2(DMF)(H_2O)_2]NO_3\cdot 2H_2O$ (**1**) and [Gd(tmbpy)$_2$(DMF)(NO_3)]·DMF·THF (**2**), in which tbpyH and tmbpyH serve as the mono-anionic tridentate chelating ligands via deprotonation of the tetrazolyl-NH. It is demonstrated that the methylation of the 2,2′-bipyridyl ring has an important influence on the molecular structures of Gd(Ⅲ) complexes, exhibiting

that two mono-coordinated H_2O molecules are replaced by one bidentate chelating nitrate. We believe that the results presented herein might provide new insight into the design and synthesis of new Ln(Ⅲ) complexes.

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