研究简报

一种镧系-过渡金属二维氰桥配合物[Nd(DMSO)$_2$(H$_2$O)$_2$][Ni(CN)$_4$]Cl (DMSO=二甲亚砜)的合成和晶体结构

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Synthesis and Crystal Structure of a Cyano-Bridged Lanthanide-Transition-Metal Complex [Nd(DMSO)$_2$(H$_2$O)$_2$][Ni(CN)$_4$]Cl (DMSO=Dimethylsulfoxide) with Two-dimensional Gridding Molecule Structure

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Abstract: The cyano-bridged bimetallic complex [Nd(DMSO)$_2$(H$_2$O)$_2$][Ni(CN)$_4$]Cl with two-dimensional gridding molecule structure was synthesized and characterized. In the complex all four cyano groups of unit Ni(CN)$_4^{2-}$ are bound to Nd^{3+} ions. The crystal data for the title complex: monoclinic, space group $P2_1/c$, a=0.780 0(3) nm, b=1.509 7(6) nm, c=1.683 2(6) nm, β=115.231(14)°, Z=4, μ=4.311 mm^{-1}, final R_1=0.020 9, wR_2=0.045 4. CCDC: 272214.

Key words: cyano-bridged complex; lanthanide-transition metal complex; DMSO

0 Introduction

There has been continued interest in cyanide-bridged lanthanide-transition-metal complexes because of their applications as precursors in the preparation of various materials, such as rare earth orthoferrites[1], electroceramic materials[2], chemical sensor materials[3], catalysis materials[4], and molecular magnets materials[5]. To the best of our knowledge, the study about tetracyanometalate complex is less than hexacyanometalate complex. In 1985, a series of rare-earth complexes having the general formula Ln$_2$[Pt(CN)$_4$]$_3$·xH$_2$O (x=18 or 21) have been reported[6]. Incorporation of organic ligands into the 4*f*-3*d* complexes can give various molecular structures. Some unusual cyano-bridged one-dimensional 4*f*-3*d* arrays derived from tetracyanometalate M(CN)$_4^{2-}$ (M=Ni, Pd, Pt) have been produced, e.g. {(DMF)$_{10}$Ln$_2$[M(CN)$_4$]$_3$}$_\infty$ (Ln=Sm, Eu, Er, Yb and M=Ni, Pd , Pt)[7]. Very recently, the pentanuclear cyano-bridged 4*f*-3*d* array [Ho(H$_2$O)$_3$(DMF)$_3$]$_2$[Ni(CN)$_4$]$_3$ was reported based on the reaction of K$_2$[Ni(CN)$_4$] and Ho(NO$_3$)$_3$·6.5H$_2$O in DMF[8]. But the 4*f*-3*d* complexes that all four cyano groups are bound as monodentate ligands have been poorly reported. Here

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we will report a novel complex $[Nd(DMSO)_2(H_2O)_2][Ni(CN)_4]Cl$ with two-dimensional gridding structure. In the complex all four cyano groups of unit $Ni(CN)_4^{2-}$ are bound to Nd^{3+} ions.

1 Experimental

1.1 Materials

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with a Perkin-Elmer 240C elemental analyzer. The infrared spectrum on KBr pellets was performed on a Nicolet Magna-IR 560 spectrophotometer in the 4 000~400 cm^{-1} regions. TGA measurement of the compound was performed in the temperature range 20~800 ℃ under nitrogen on a universal V2.6D TA instrument.

1.2 Synthesis of the $[Nd(DMSO)_2(H_2O)_2][Ni(CN)_4]Cl$

$NdCl_3·6H_2O$ (0.79 g, 2.2 mmol), DMSO (0.32 mL, 4.4 mmol) and $K_2[Ni(CN)_4]$ (0.53 g, 2.2 mmol) reacted in the molar ratio of 1∶2∶1 in deionized water. Slow evaporation of the resultant pink mixture in the dark at room temperature gave well-shaped pink single crystal. Anal. Calcd(%) for $C_8H_{16}ClN_4NdNiO_4S_2$ (534.77): C,17.97; N,10.48; H,3.02. Found(%): C, 17.82; N, 10.34; H, 3.25.

1.3 X-ray structure determination

The data collections of the title complex were performed on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 20 mA using Mo $K\alpha$ radiation (λ=0.071 073 nm) at 293 K. A total of 10 026 independent reflections were measured to give 3 609 independent reflections (R_{int}=0.022 7). Semiempirical absorption correction was applied using the SADABS program. The structure was solved by the direct method (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97) on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Weighted R-factors, wR, and all goodness of fit (S) values are based on F^2. The weighting scheme is $w=1/[\sigma^2(F_o^2)+(0.006\ 8P)^2+2.88P]$ where $P=(F_o^2+2F_c^2)/3$. The crystal data and the experimental details for structural analyses are summarized in Table 1.

CCDC: 272214.

Table 1 Crystallographic data for the title complex

Empirical	$C_8H_{16}ClN_4NdNiO_4S_2$
Formula	534.77
Temperature / K	293(2)
Wavelength / nm	0.071 073
Crystal system	Monoclinic
Space group	$P2_1/c$
a / nm	0.780 0(3)
b / nm	1.509 7(6)
c / nm	1.683 2(6)
β / (°)	115.231(14)
Volume / nm^3	1.793 0(12)
Z	4
Density / ($Mg·m^{-3}$)	1.981
F(000)	1 044
Crystal size / mm	0.20 × 0.18 × 0.12
Reflections collected	10 026
Independent reflections	3 609
Number of parameters	194
Goodness of fit on F^2 (s)	1.194
Final R indices [$I>2\sigma(I)$]	R_1=0.020 9, wR_2=0.045 4
R indices (all data)	R_1=0.023 6, wR_2=0.046 2

2 Results and discussion

2.1 IR characterizations

The IR spectrum of the title complex shows three strong bands at 2 139.8 cm^{-1}, 2 153.0 cm^{-1}, 2 166.3 cm^{-1} assigned to $\nu_{C\equiv N}$; The sharp bonds at 963.6 cm^{-1}, 1 007.4 cm^{-1}, 1 019.2 cm^{-1} are attributed to $\nu_{S=O}$.

2.2 Thermal study

Thermal gravimetric analysis (TGA) reveals that the complex can absorb water molecule as a consequence of the gridding structure[9,10]. The TGA shows a weight loss of 3.8% in the temperature range 22~200 ℃, corresponding to one water molecules (calcd 3.3%), probably one coordinated water molecule. Then the weight of loss 15.4% in the range of 200 to 350 ℃ corresponds to the loss of the other coordinated water molecule and 0.75DMSO molecule (calcd 15.4%). This partially dehydrated material go on decomposing up to 800 ℃.

2.3 Crystal structure

The selected bond distances and angles for $[Nd(DMSO)_2(H_2O)_2][Ni(CN)_4]Cl$ are shown in Table 2. Table 3 gives the distances and angles related with the hydrogen bonding. Fig.1 is a perspective view of

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

Nd(1)-O(1)	0.238 8(2)	Ni(1)-C(4)#1	0.185 8(3)	N(1)-C(1)	0.114 4(4)
Nd(1)-O(2)	0.2428(2)	Ni(1)-C(1)	0.186 3(3)	N(2)-C(2)	0.114 2(4)
Nd(1)-O(4)	0.246 7(2)	Ni(1)-C(3)#2	0.187 3(3)	C(2)-Ni(1)#4	0.187 5(3)
Nd(1)-O(3)	0.252 2(2)	Ni(1)-C(2)#3	0.187 5(3)	N(3)-C(3)	0.114 6(4)
Nd(1)-N(4)	0.252 7(3)	S(1)-O(1)	0.151 8(2)	C(3)-Ni(1)#5	0.187 3(3)
Nd(1)-N(1)	0.253 2(3)	S(1)-C(5)	0.176 6(4)	N(4)-C(4)	0.114 5(4)
Nd(1)-N(2)	0.256 0(3)	S(2)-C(7)	0.177 2(5)	C(4)-Ni(1)#6	0.185 8(3)
Nd(1)-N(3)	0.258 3(3)	O(3)-H(3A)	0.085 01	C(5)-H(5A)	0.096 00
O(1)-Nd(1)-O(2)	132.11(8)	O(2)-Nd(1)-N(2)	138.05(9)	C(1)-Ni(1)-C(2)#3	89.36(14)
O(1)-Nd(1)-O(4)	143.82(8)	O(4)-Nd(1)-N(2)	107.10(9)	C(3)#2-Ni(1)-C(2)#3	92.85(14)
O(2)-Nd(1)-O(4)	70.10(9)	O(3)-Nd(1)-N(2)	67.99(9)	N(1)-C(1)-Ni(1)	179.1(3)
O(1)-Nd(1)-O(3)	135.67(8)	N(4)-Nd(1)-N(2)	88.96(10)	N(2)-C(2)-Ni(1)#4	174.8(3)
O(2)-Nd(1)-O(3)	71.47(8)	N(1)-Nd(1)-N(2)	148.90(9)	N(3)-C(3)-Ni(1)#5	173.8(3)
O(4)-Nd(1)-O(3)	73.24(8)	O(1)-Nd(1)-N(3)	76.98(9)	N(4)-C(4)-Ni(1)#6	178.4(3)
O(1)-Nd(1)-N(4)	74.41(9)	O(2)-Nd(1)-N(3)	129.18(9)	O(1)-S(1)-C(5)	105.71(18)
O(2)-Nd(1)-N(4)	74.00(9)	O(4)-Nd(1)-N(3)	67.96(9)	C(5)-S(1)-C(6)	99.5(2)
O(4)-Nd(1)-N(4)	140.57(9)	O(3)-Nd(1)-N(3)	120.18(9)	S(1)-O(1)-Nd(1)	136.14(14)
O(3)-Nd(1)-N(4)	80.45(9)	N(4)-Nd(1)-N(3)	151.31(9)	C(1)-N(1)-Nd(1)	170.8(3)
O(1)-Nd(1)-N(1)	75.11(9)	N(1)-Nd(1)-N(3)	81.56(10)	C(2)-N(2)-Nd(1)	159.6(3)
O(2)-Nd(1)-N(1)	71.60(9)	N(2)-Nd(1)-N(3)	82.00(10)	C(3)-N(3)-Nd(1)	158.8(3)
O(4)-Nd(1)-N(1)	90.81(9)	C(4)#1-Ni(1)-C(1)	88.01(14)	C(4)-N(4)-Nd(1)	178.4(3)
O(3)-Nd(1)-N(1)	142.88(9)	C(4)#1-Ni(1)-C(3)#2	89.75(14)	S(1)-C(5)-H(5A)	109.5
N(4)-Nd(1)-N(1)	92.97(10)	C(1)-Ni(1)-C(3)#2	177.69(13)	H(5A)-C(5)-H(5B)	109.5
O(1)-Nd(1)-N(2)	75.56(9)	C(4)#1-Ni(1)-C(2)#3	176.72(14)		

Symmetry transformations used to generate equivalent atoms: #1: $x-1$, y, z; #2: $-x-1$, $y-1/2$, $-z-1/2$; #3: $-x$, $y-1/2$, $-z-1/2$; #4: $-x$, $y+1/2$, $-z-1/2$; #5: $-x-1$, $y+1/2$, $-z-1/2$; #6: $x+1$, y, z.

Table 3　Distances (nm) and angles (°) involving hydrogen bonding

D-H	A	*d*(D-H)	*d*(H···A)	∠DHA	*d*(D···A)
O3-H3A	Cl1^{i}	0.085 0	0.258 9	121.84	0.312 3
O3-H3B	Cl1^{ii}	0.085 0	0.244 6	154.76	0.323 5
O4-H4B	Cl1^{iii}	0.085 0	0.253 4	133.22	0.317 7
O4-H4A	Cl1^{iv}	0.085 0	0.238 5	156.14	0.318 1

Symmetry transformations: ^{i} x, $-y-1/2$, $z+1/2$; ^{ii} $-x+1$, $y+1/2$, $-z-1/2$; ^{iii} $-x$, $y+1/2$, $-z-1/2$; ^{iv} x, $-y-1/2$, $z+1/2$.

[Nd(DMSO)$_2$(H$_2$O)$_2$][Ni(CN)$_4$]Cl molecule with atomic labeling scheme. The crystal structure of the title complex along *c*-axis direction is depicted in Fig.2. Fig.3 gives the packing diagram of the complex.

X-ray single-crystal structure analysis revealed that the 2D polymer layer [Nd(DMSO)$_2$(H$_2$O)$_2$][Ni(CN)$_4$]Cl consists of square-planar Ni^{2+} and eight-coordinate Nd^{3+} ions alternately linked by the bridging cyano groups. The asymmetric unit of the complex consists of one independent $[Ni(CN)_4]^{2-}$ unit, one independent of Nd^{3+} unit, two DMSO, two water molecules and one Cl^- ion. All four cyano groups of $Ni(CN)_4^{2-}$ unit are involved in the coordination to adjacent Nd^{3+} ions. The Ni atom exhibits a square-planar environment with four cyano carbon atoms, the Ni-C bonds are in the range of 0.185 8(3) and 0.187 5(3) nm, and the angles between two proximate C atoms and Ni(1) atom are listed: C(4)#1-Ni(1)-C(1)=88.01(14)°, C(4)#1-Ni(1)-C(3)#2=89.75(14)°, C(1)-Ni(1)-C(2)#3=89.36(14)°, C(3)#2-Ni(1)-C(2)#3=92.85(14)° (where #1denotes the transformation $x-1$, y, z and #2 denotes $-x-1$, $y-1/2$, $-z-1/2$ and #3 denotes $-x$, $y-1/2$, $-z-1/2$). In con-

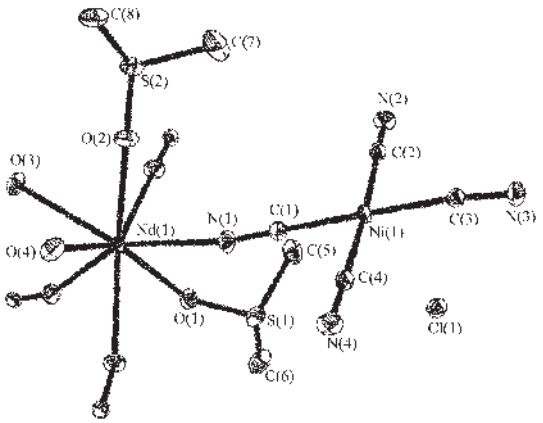

Fig.1 Perspective view of $[Nd(DMSO)_2(H_2O)_2][Ni(CN)_4]Cl$ with the atomic numbering scheme

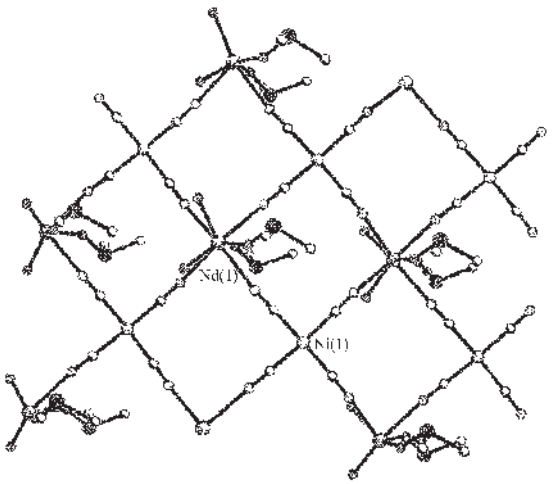

Fig.2 Crystal structure of $[Nd(DMSO)_2(H_2O)_2][Ni(CN)_4]Cl$ along *c*-axis

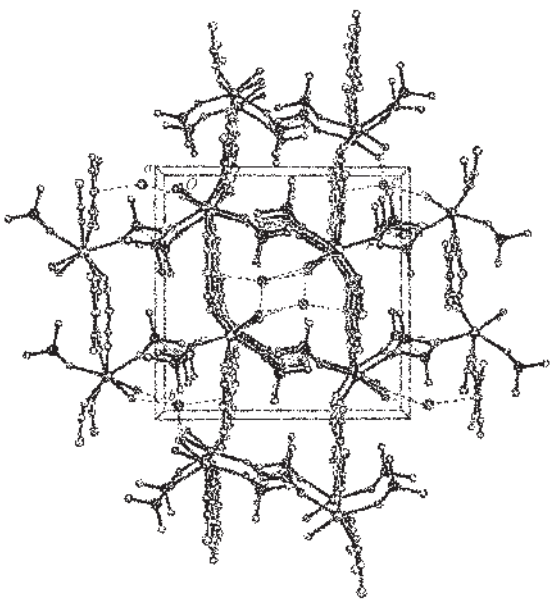

Fig.3 Packing diagram of the title complex

trast, the Nd^{3+} ion is connected to four cyano nitrogens and four oxygen atoms of two DMSO and two water molecules. The bridging cyanides coordinate to the Nd^{3+} ions in four different fashions: two nearly linear C(1)-N(1)-Nd(1)=170.8(3)°, C(4)-N(4)-Nd(1)=178.4(3)° and two bend C(2)-N(2)-Nd(1)=159.6(3)°, C(3)-N(3)-Nd(1) =158.8(3)°.The Nd-O bond distances range from 0.238 8(2) to 0.252 2(2) nm, and the Nd-N bond lengths range from 0.252 7(3) to 0.258 3(3)nm. The adjacent Ni⋯Nd distances are 0.553 9 nm for Ni(1)⋯Nd(1), 0.557 7 nm for Ni(1)#4⋯Nd(1), 0.560 2 nm for Ni(1)#5⋯Nd(1) and 0.553 nm for Ni(1)#6⋯Nd(1).

The crystal structure of the title complex along *c*-axis reveals that the structure consists of neutral layers with relatively regulate Ni_2Nd_2 rectangles. The Ni^{2+} and Nd^{3+} ions are situated at the four corners. All the Ni^{2+} ions are coplanar, but all the Nd^{3+} ions deviated from the plane. Between the closer layers, the Cl^- ions interact with the coordinated water molecules through hydrogen bonds to connect the two layers (Fig.3).

In conclusion, the structure of the complex $Nd(DMSO)_2(H_2O)_2][Ni(CN)_4]Cl$ is novel. First, all four cyano groups of unit $Ni(CN)_4^{2-}$ are bound to Nd^{3+} ions, which is difficult to have coplanar structure of $Ni(CN)_4^{2-}$. Second, the molecule DMSO is an infrequent ligand. Of course, the complex may have potential appliance prospect in catalysis and molecular magnets.

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