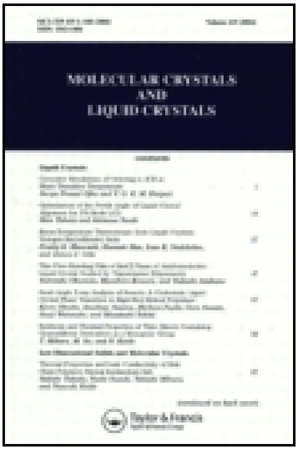

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Structures and Photo-Induced Magneto-Optic Faraday Effect in Rare Earth Nitroprussides

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Structures and Photo-Induced Magneto-Optic Faraday Effect in Rare Earth Nitroprussides

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Four novel one dimensional 4f-3d molecules $PrFe(CN)_5(NO)(phen)_2$-$(NO_3)(H_2O)\bullet H_2O$(**A**) and $REFe(CN)_5(NO)(phen)_2(NO_3)(H_2O)\bullet 0.5H_2O$ (RE=Tb(**B**), Eu(**C**), Y(**D**)) have been designed and synthesized. Their structures were determined using single-crystal X-ray diffraction method. They all consist of zigzag chain structures with the shortest intrachain distance of RE-Fe about 5.5Å. The Mössbauer spectra of solid state sample **B** suggest no valence change of Fe atom under irradiation. Magnetic circular dichroism (MCD) spectra of all samples in dimethyl sulphoxide (DMSO) solution show two strong $[Fe(III)(CN)_6]^{3-}$ characteristic bands after irradiation by Xe lamp due to a photochemical reaction.

Keywords: rare earth nitroprussides; structure; photoreaction; UV & MCD

INTRODUCTION

Designing and making functional materials in molecular level for molecular electronic devices is a great challenge of our age. Transition-metal nitrosyl complexes, such as sodium nitroprusside $Na_2Fe(CN)_5(NO)\cdot 2H_2O$, have been found to exist extremely long-lived electronic excited states which can induced by light in the wavelength range of 350-580nm under liquid nitrogen temperature, and such complexes were also used as building blocks to form new molecular materials[1]. The photochemical behavior of these complexes in water and non-aqueous solvents has also attracted much interest for many years[2-4]. Photooxidation of the metal center and solvation of NO ligand was reported to be the major mode in water or non-aqueous solution, whereas photoreduced production of iron(I) species were also generated in some non-aqueous solutions[3]. Up to now, the structures and properties of single crystals, crystalline powders or solutions of nitrosylpentacyanoferrates of different cations, including alkali metals, alkaline earth metals and other bivalent ions have been reported[5]. But no nitroprusside complex of rare earth or other trivalent metal was investigated. In our research of low dimensional 4f-3d magnetic molecular materials, we designed and synthesized some novel one dimensional molecules using sodium nitroprusside as the starting material, and found that their electronic and MCD spectra in DMSO solution changed upon irradiation.

EXPERIMENTAL SECTION

Synthesis of the Complexes

$RE(NO_3)_3$ (RE = Pr, Eu, Tb, Y) was made by RE_2O_3 (99.99%) and HNO_3 (A.R.). $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ (Na_2Np) and 1,10-phenanthroline (phen) were reagent grade (A.R.) and used without further purification. The title complexes **A**, **B**, **C** and **D** were prepared by mixing an aqueous solution of Na_2Np (1mmol) and an alcohol solution of phen (2mmol), and adding aqueous solution of $RE(NO_3)_3$ (1mmol) slowly without stirring. The result solution was kept in the dark. Orange single crystals suitable for X-ray diffraction study were obtained by slow evaporation of the solution at room temperature.†

†Anal. Calcd for $PrFeC_{29}N_{11}O_6H_{20}$(**A**) C: 42.68 H: 2.45 N: 18.89, Found C: 41.43 H: 2.57 N: 18.05. Anal. Calcd for $TbFeC_{29}N_{11}O_{5.5}H_{19}$(**B**) C: 42.21 H: 2.30 N: 18.68 Found C: 42.12 H: 2.26 N: 18.65. Anal. Calcd for $EuFeC_{29}N_{11}O_{5.5}H_{19}$(**C**) C: 42.60 H: 2.33 N: 18.85, Found C: 41.75 H: 2.58 N: 18.03. Anal. Calcd for $YFeC_{29}N_{11}O_{5.5}H_{19}$(**D**) C: 46.14 H: 2.52 N: 20.42, Found C: 46.11 H: 2.72 N: 19.84.

Physical Measurements

IR spectroscopic analyses were carried out on a Nicolet 750 FTIR spectrometer. Thermogravimetric analysis (TGA) was made by Dupont 1090 thermobalance under pressed atmosphere. UV-Vis spectra were recorded using a Shimadzu UV-1206 spectrophotometer. The ^{57}Fe Mössbauer data at room temperature were recorded on a constant acceleration spectrometer with a source ^{57}Co(Rh) of 10mCi. MCD spectra were measured using a JASCO model 500C instrument.

Determination of Crystal Structure

The suitable single crystals of **A** and **B** were mounted on a Siemens P4 and **D** on an Enraf-Nonius CAD4 mach3 diffractometer equipped with a graphite monochromator. All reflection data were collected at 292K using Mo Kα radiation (λ=0.71073Å) and ω-2θ scanning technique. Intensity data were corrected for LP factors and ψ-scan absorption[6]. The structure was solved by direct methods and refined by full-matrix least-square techniques[7]. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were located by riding model and fixed isotropic U. The crystallographic data of **A**, **B** and **D** are summarized in Table 1.

TABLE 1 Crystallographic data for **A**, **B** and **D**

	A	**B**	**D**
Empirical formula	$C_{29}H_{20}FeN_{11}O_6Pr$	$C_{29}H_{19}FeN_{11}O_{5.5}Tb$	$C_{29}H_{19}FeN_{11}O_{5.5}Y$
Formula weight	815.32	824.33	754.30
Temperature(K)	293(2)	293(2)	293(2)
Wave length(Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pna2	C2/c	C2/c
a(Å)	20.718(9)	13.442(3)	13.429(3)
b(Å)	17.708(7)	15.766(4)	15.768(3)
c(Å)	9.165(5)	14.539(3)	14.513(3)
β(°)		94.92(2)	94.77(3)
Volume(Å^3)	3362(3)	3070.0(12)	3062.5(11)
Z	4	4	4
Dc (Mg/m^3)	1.611	1.768	1.616
Abs. Coefficient(mm^{-1})	1.921	2.816	2.418
Transmission factor	0.198-0.411	0.135-0.486	0.9423-0.9985
F(000)	1616	1608	1496
Crystal size(mm^3)	0.70 x 0.40 x 0.25	0.2 x 0.2 x 0.4	0.2 x 0.2 x 0.3

Theta range(°)	1.51 to 27.54	2.00 to 30.01	2.00 to 27.0
Index ranges	$-1 \le h \le 26$, $-23 \le k \le 1$, $-1 \le l \le 11$	$-1 \le h \le 18$, $-1 \le k \le 22$, $-20 \le l \le 20$	$-17 \le h \le 17$, $-20 \le k \le 0$, $-18 \le l \le 18$
Collected/unique data	5123/4581	5360/4492	4153/3349
R(int)	0.0284	0.0521	0.0578
Completeness to 2θ	99.6%	99.9%	100.0%
Data/restraints/parameters	4581/7/434	4492/0/234	3349/0/233
Goodness-of-fit on F^2	0.963	1.051	1.155
Final R indices [$I>2\sigma(I)$]	*R_1=0.0566, **wR_2=0.1432	R_1=0.0707, wR_2=0.1877	R_1 = 0.0503, wR_2 = 0.1389
Rindices (all data)	R_1=0.0764, wR_2=0.1552	R_1=0.0774, wR_2=0.1923	$R1$=0.0713 wR_2=0.1481
Largest diff. Peak and hole	2.250, -2.392e Å^{-3}	2.929, -4.775eÅ^{-3}	1.563, -1.300 eÅ^{-3}

*$R_1=\Sigma||F_0|-|F_c||/\Sigma|F_0|$ **$wR_2=\{\Sigma[w(F_0-F_c)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$

RESULTS AND DISCUSSIONS

Thermogravimetric Analysis and IR Spectra

TGA shows that the decomposition process contains two steps. Before 350°C, all waters and a phen are lost with a cumulative loss of 26.85% (calc.26.49%) for **A** and 23.56% (calc.25.11%) for **B**, respectively. With the increase of the temperature, the complexes are decomposed completely and oxidized with the remaining weight of 28.73% (calc.29.03%) for **A** and 34.94% (calc.31.62%) for **B** according to Ln_2O_3 and Fe_2O_3, respectively.

Comparing with IR of Na_2Np, the strong bands of $\nu_{C\equiv N}$ in the complexes **A** and **B** become more complicate, located at 2154, 2145, 1919cm^{-1} for **A** and 2142, 2171, 1905 cm^{-1} for **B**, respectively, due to bridging of cyanide groups. The bands at 1656-1539, 1424-1495cm^{-1} for **A** and 1591, 1578, 1522, 1450, 1426cm^{-1} for **B** are $\nu_{C=N}$ and $\nu_{C=C}$ of phen, respectively. Strong sharp peak at 1384cm^{-1} belongs to $\nu_{O=N}$. The peak of Fe-CN (ν) at approximately 417cm^{-1} shows a little red shift compared to the situation in Na_2Np.

Description of the Structures

Molecular structure of $PrFe(CN)_5(NO)(phen)_2(NO_3)(H_2O)\cdot H_2O$(A): The ORTEP view of **A** is shown in Figure 1. Selected bond lengths and angles are listed in Table 2. Pr(III) is nine coordinated by four N atoms of two phen molecules, two O atoms of bidentated NO_3^- group, one O atom of water molecule and two bridging N atoms of cyano groups, forming a mono-capped square antiprism. Its two faces are defined by N2, N3, N4, O1W and N1, N6, O2, N9A, the cap position is occupied by O4. Fe(II) ion is six coordinated by five CN groups and one NO group and has an approximately octahedral coordination environment. The mean distance of Fe-C is 1.933Å and Fe-N is 1.663Å, which is corresponding to those in Na_2Np[8]. The average bond lengths of C-N and N-O are 1.14Å and 1.12Å, respectively, which are in agreement with the values found for the other cyano and nitrosyl compounds[8-10]. Each Fe is linked to two Pr atoms through two cyano groups forming an infinite alternating chain as shown in Figure 2. The average angles of linked Pr-N-C and Fe-C-N are 156.5 and 176.8°, respectively. The shortest intrachain distances of Pr-Fe are 5.514(3) and 5.535(3)Å. The interchain distances of metal ions in the complex are larger than 8Å.

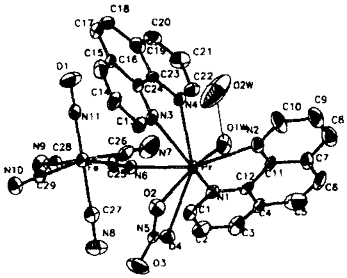

FIGURE 1 The ORTEP view of PrFe-$(CN)_5(NO)(phen)_2(NO_3)(H_2O)\cdot H_2O$ (30% probability displacement ellipsoids.)

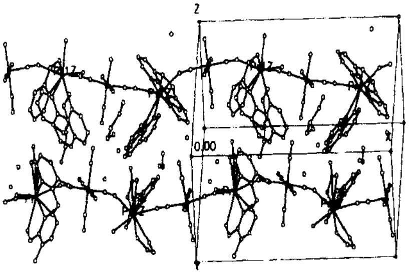

FIGURE 2 The packing of 1-D zigzag chain in a unit cell of **A**

TABLE 2. Selected bond lengths [Å] and angles [deg] for **A**

Bond lengths

Pr-O(1W)	2.498(8)	Pr-N(1)	2.656(9)
Pr-O(2)	2.537(11)	Fe-N(11)	1.663(12)
Pr-N(9A)	2.568(10)	Fe-C(27)	1.924(15)
Pr-O(4)	2.584(10)	Fe-C(26)	1.925(17)
Pr-N(6)	2.610(9)	Fe-C(28)	1.928(11)
Pr-N(3)	2.615(9)	Fe-C(25)	1.938(11)
Pr-N(4)	2.639(10)	Fe-C(29)	1.952(14)
Pr-N(2)	2.652(11)	N(6)-C(25)	1.124(13)

Angles

O(1W)-Pr-O(2)	82.0(4)	N(3)-Pr-N(4)	63.0(3)
O(1W)-Pr-N(9A)	72.5(3)	O(1W)-Pr-N(2)	77.9(4)
O(2)-Pr-N(9A)	80.6(4)	O(2)-Pr-N(2)	147.9(4)
O(1W)-Pr-O(4)	122.9(4)	N(9)A-Pr-N(2)	69.7(4)
O(2)-Pr-O(4)	51.3(3)	O(4)-Pr-N(2)	123.5(3)
N(9)A-Pr-O(4)	69.4(4)	N(6)-Pr-N(2)	127.9(3)
O(1W)-Pr-N(6)	143.4(3)	N(3)-Pr-N(2)	119.6(3)
O(2)-Pr-N(6)	82.2(4)	N(4)-Pr-N(2)	76.1(3)
N(9)A-Pr-N(6)	136.3(4)	O(1W)-Pr-N(1)	137.6(3)
O(4)-Pr-N(6)	68.4(3)	O(2)-Pr-N(1)	123.9(3)
O(1W)-Pr-N(3)	68.8(3)	N(9)A-Pr-N(1)	79.1(3)
O(2)-Pr-N(3)	74.6(3)	O(4)-Pr-N(1)	72.6(3)
N(9)A-Pr-N(3)	136.2(3)	N(6)-Pr-N(1)	77.8(3)
O(4)-Pr-N(3)	116.9(3)	N(3)-Pr-N(1)	144.6(3)
N(6)-Pr-N(3)	75.2(3)	C(25)-N(6)-Pr	154.8(10)
O(1W)-Pr-N(4)	100.3(4)	C(28)-N(9)-Pr(B)	158.2(13)
O(2)-Pr-N(4)	132.6(3)	N(4)-Pr-N(1)	85.8(3)
N(9)A-Pr-N(4)	145.7(4)	N(2)-Pr-N(1)	62.8(3)
O(4)-Pr-N(4)	134.4(3)	N(6)-C(25)-Fe	178.9(10)
N(6)-Pr-N(4)	68.0(4)	N(9)-C(28)-Fe	174.6(14)

Symmetry transformations used to generate equivalent atoms:
A: x-1/2, -y+3/2, z   B: x+1/2, -y+3/2, z

Molecular structures of $REFe(CN)_5(NO)(phen)_2(NO_3)(H_2O) \cdot 0.5H_2O$ (RE = Tb(B), Y(D)): The crystals of **B** and **D** are isomorphous shown in Figure 3, and selected bond distances and angles are listed in Table 3. RE is also nine coordinated by six N atoms and three O atoms. The coordination polyhedron around RE is a mono-capped square antiprism with N1, N2, N3, O1 and N1A, N2A, N3A, O1A forming the two faces respectively, and water molecule occupying the cap position. Since the coordinated water molecule is symmetry related with NO_3^-, the occupancy for each was refined to 0.5. Thus, there is a total of three oxygen atoms coordinated to every RE atom, and the mean distance of RE-O is 2.55Å in **B** and 2.56Å in **D**. The molecular structures of **B** and **D** show higher symmetry than that of **A** due to the space effect caused by smaller ion radius of Tb^{3+} and Y^{3+} comparing with Pr^{3+}. Fe1 atom

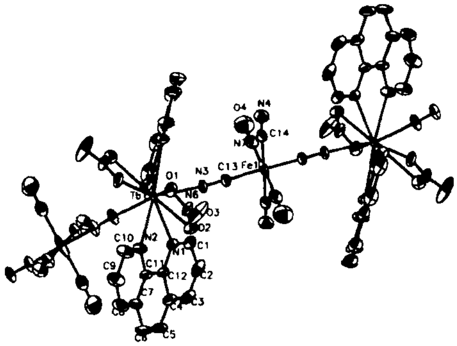

FIGURE 3 ORTEP drawing of entire molecule of $TbFe(CN)_5(NO)(phen)_2(NO_3)(H_2O)\cdot 0.5H_2O$ (30% probability displacement ellipsoids.)

locates at the symmetry center. The average distance of Fe-C in **B** and **D** is around 1.91Å, consistent with that in **A**. While the distance of Fe-N is 1.864 and 1.878Å for **B** and **D**, clearly larger than that in **A** and other nitroprusside compounds. This may be due to the statistics of N-O and C-N groups by the symmetryoperation, which make the distances of Fe-N and its symmetry related Fe-C uniformity. RE and Fe are connected through two CN groups forming a zigzag chain with related angles of N-C-Fe, C-N-RE and N-RE-N being 179.4, 176.3 and 138.9° for **B**, and 178.7, 175.8 and 138.9° for **D**, respectively. The intrachain distances of RE-Fe in **B** and **D** are 5.491 and 5.471Å, respectively.

TABLE 3. Seleted bond lengths [Å] and angles [deg] for **B** and **D**.

Bond Lengths

Tb(1)-O(1)	2.400(6)	2.365(4)	Fe(1)-C(13)	1.909(7)	1.919(5)
Tb(1)-N(3)	2.443(6)	2.420(4)	Fe(1)-C(14)	1.941(8)	1.932(5)
Tb(1)-N(2)	2.522(6)	2.517(4)	O(4)-N(7)	1.105(17)	1.085(9)
Tb(1)-N(1)	2.538(6)	2.517(4)	N(3)-C(13)	1.142(10)	1.138(6)
Tb(1)-O(2)	2.691(15)	2.766(10)	N(4)-C(14)	1.136(12)	1.133(7)
Fe(1)-N(7)	1.869(13)	1.878(8)	N(6)-O(3C)	1.80(2)	1.827(13)
Fe(1)-C(15B)	1.869(13)	1.878(8)			

Angles

O(1)-Tb(1)-O(1A)	68.5(5)	69.4(2)	O(1)-Tb(1)-N(1)	115.4(2)	114.8(1)
O(1)-Tb(1)-N(3)	79.7(3)	79.3(2)	N(3)-Tb(1)-N(1)	73.1(2)	73.4(1)
O(1A)-Tb(1)-N(3)	139.9(3)	139.7(2)	N(2)-Tb(1)-N(1)	65.6(2)	65.7(1)
N(3A)-Tb(1)-N(3)	138.9(2)	138.9(2)	N(2)-Tb(1)-O(2)	60.4(4)	60.6(2)
O(1)-Tb(1)-N(2)	80.2(2)	79.3(2)	N(3)-Tb(1)-O(2A)	128.4(4)	128.7(2)
O(1A)-Tb(1)-N(2)	79.3(2)	79.9(1)	O(1)-Tb(1)-O(2A)	104.2(3)	105.4(2)
N(3A)-Tb(1)-N(2)	70.3(2)	70.6(2)	O(4)-N(7)-Fe(1)	177.1(12)	178.7(8)
N(3)-Tb(1)-N(2)	119.3(3)	119.2(2)	N(1)-Tb(1)-O(2A)	138.5(3)	137.8(2)

N(2)-Tb(1)-N(2A)	155.1(3)	154.5(2)	O(2)-Tb(1)-O(2A)	147.6(5)	148.5(3)
O(1)-Tb(1)-N(1A)	142.5(2)	142.9(2)	C(13)-N(3)-Tb(1)	176.3(7)	175.8(5)
N(3)-Tb(1)-N(1A)	76.5(3)	76.5(2)	N(3)-C(13)-Fe(1)	179.4(9)	178.7(6)
N(2)-Tb(1)-N(1A)	137.1(2)	137.5(1)	N(2A)-Tb(1)-O(2)	111.9(4)	111.8(2)
N(1A)-Tb(1)-N(1)	84.7(3)	84.7(2)	O(1)-Tb(1)-O(2)	45.0(3)	44.6(2)
N(3)-Tb(1)-O(2)	64.8(4)	64.2(2)	N(1)-Tb(1)-O(2)	70.3(3)	70.2(2)

Symmetry transformations used to generate equivalent atoms:
A: -x,y,-z+1/2; B: -x+1/2,-y+1/2,-z; C: -x,-y,-z

Mössbauer Study

The Mössbauer parameters isomer shift (IS) and quadrupole splitting (QS) of powderized single crystal samples for Na_2Np and **B** were measured at room temperature using α-Fe as the standard sample. The IS and QS of Na_2Np are -0.532mm/s and 1.693mm/s respectively, consistent with the reported data before[11]. For freshly prepared sample of **B**, IS data is -0.552mm/s, a little change from Na_2Np. This can be easily understood from the similar coordination environment and valence of Fe in **B** and Na_2Np[12]. The QS of **B** is 1.915mm/s, a slightly different from Na_2Np due to the small change of symmetry around Fe atom. When solid sample of **B** was irradiated by Xe lamp at 450nm for two hours, the value of IS and QS are -0.550 and 1.909 mm/s, respectively. No evident change occurs in both its color and Mössbaüer spectrum, suggesting that the valence of Fe in **B** is kept +2 before and after irradiation.

Absorption and MCD Spectra of the complexes in DMSO

Two sets sample of complexes **A**, **B**, **C**, **D** and Na_2Np were dissolved in DMSO (0.0025mol/L). One set is stored in a dark box at room temperature and the other is irradiated by Xe Lamp of 450nm.

The absorption spectra of the freshly prepared complexes and Na_2Np in DMSO are similar to the ones of Na_2Np in water[3]. After irradiation, the band at about 393nm which can be assigned to d_{xz}, $d_{yz} \rightarrow \pi^*(NO)$ of Fe(II)[14] was disappeared and two new bands at about 319nm and 427nm were observed in all samples. With increase of irradiation time, the two bands slowly shift to the lower energy direction and the intensity of the peaks increased gradually. We assign these new bands as the transitions n→π* of phen and CN→Fe(III) LMCT transition of $[(NC)_5Fe^{III}]^{2-}$ [2]. This indicates that Fe(II) in the samples is photooxided to Fe(III) under irradiation. The obvious difference of irradiated production between Na_2Np and rare earth nitroprussides is that a new bond appears at about 630-670nm only in Na_2Np, which was considered as the contribution of the pentacoordinated iron(I) species[2,3,16].

No CD and MCD signal was observed in the freshly prepared samples. After irradiation, there are two strong MCD bonds appearing in all samples shown in Figure 4, one positive at 420nm and the other negative at 320-330nm, a little red shifting compared to the characteristic bands found in $[Fe(III)(CN)_6]^{3-}$ of aqueous solution and PVA film (417 and 303nm respectively)[15] due to solvent effect. The common characteristic of these bands in different samples is that the MCD spectrum shows its maximum at the same position of its absorption maximum, which may arise predominantly from the Faraday term ($B+C/kT$). There is no evident influence to the intensity of MCD signal for different rare earth ions.

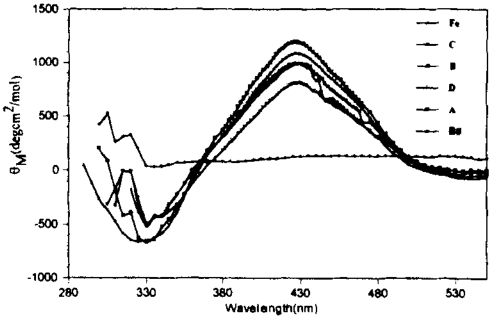

FIGURE 4 MCD spectra of Na_2Np and **A**, **B**, **C** and **D** in DMSO solution after irradiation by Xe lamp (**B**#: fresh prepared **B**; Fe: Na_2Np)

Based on the present results, the photo-magnetic properties of the complexes may be summarized as follows: (1) The irradiation at 450nm does not cause valence change of Fe for solid state samples of rare earth nitroprusside under room temperature; (2) A photooxidation reaction of

Fe(II)→Fe(III) happened in DMSO solution of Na_2Np and rare earth complexes.

Further investigation on the photo-magnetic behavior of crystalline solid state samples of rare earth nitroprussides under low temperature is in progress.

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