



一种具有一维链状结构的 4f-3d 双核配合物 [Eu(DMSO)₃(H₂O)₃Cr(CN)₆]·H₂O(DMSO=二甲亚砜) 的合成、晶体结构和磁性研究

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Synthesis, Crystal Structure, Magnetic Properties of a Bimetallic 4f-3d Array [Eu(DMSO)₃(H₂O)₃Cr(CN)₆]·H₂O(DMSO=Dimethylsulfoxide) with One-Dimensional Chain Molecular Structure

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Abstract: A new cyano-bridged complex [Eu(DMSO)₃(H₂O)₃Cr(CN)₆]·H₂O with one-dimensional chain molecular structure was synthesized and characterized. The crystal data for the title complex: orthorhombic, $P2_12_12_1$, $a=0.972\ 2(3)$ nm, $b=1.489\ 5(4)$ nm, $c=1.748\ 6(5)$ nm, $Z=4$, $\mu=3.171\ \text{mm}^{-1}$, final $R_1=0.020\ 4$, $wR_2=0.043\ 4$. From magnetic susceptibility measurements the complex was found to exhibit a weak ferromagnetic interaction between the Eu (III) and Cr(III) atoms. CCDC: 272212.

Key words: 4f-3d complex; cyano-bridged complex; magnetic properties

0 Introduction

In the last decade, cyano-bridged prussian blue analogues^[1-12] have been intensively studied from the viewpoint of use as functionalized molecule-based magnets^[13-18]. For typical magnetic materials such as metal alloys and metal oxides, rare-earth metals play an important role, because rare-earth metals can cause a large magnetic anisotropy in magnets due to their orbital angular momentum. These type complexes are free assemblies to form variety molecular magnet com-

plexes and possess high magnetic-ordering temperature. The magnetic susceptibility of $\text{LnM}(\text{CN})_6 \cdot n\text{H}_2\text{O}$ ($\text{M}=\text{Fe}$ or Cr , $n=4$ or 5)^[19] and $\text{LnCr}(\text{CN})_6 \cdot n\text{H}_2\text{O}$ ($\text{Ln}=\text{Nd}$, Sm , Gd , Tb , Dy , Ho , Er , Tm) have been measured. Incorporation of organic ligands into the 4f-3d complexes can give various molecular structures^[20-22]. Some unusual cyano-bridged one-dimensional or two-dimensional 4f-3d arrays have been produced, in which DMF molecules were as a capping ligand. e.g. $[\text{Sm}(\text{DMF})_4(\text{H}_2\text{O})_4\text{Fe}(\text{CN})_6] \cdot \text{H}_2\text{O}$ ^[23], $[\text{Ln}(\text{DMF})_4(\text{H}_2\text{O})_3\text{Fe}(\text{CN})_6] \cdot \text{H}_2\text{O}$ ($\text{Ln}=\text{lanthanide ions other than Sm and$

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Nd)^[21], [Gd(DMF)₂(H₂O)₃Cr(CN)₆]·H₂O^[24], and [Sm(DMF)_n(H₂O)₂Cr(CN)₆]·H₂O (*n*=2, 4)^[25]. Here we will report a new bimetallic complex [Eu(DMSO)₃(H₂O)₃Cr(CN)₆]·H₂O, and magnetic susceptibility measurements the complex was found to exhibit a weak ferromagnetic interaction between the Eu(III) and Cr(III) atoms.

1 Experimental

1.1 Materials

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with a Perkin-Elmer 240C elemental analyzer. The infrared spectroscopies on KBr pellets were performed on a Nicolet Magna-IR 560 spectrophotometer in the 4 000~400 cm⁻¹ region. Magnetic susceptibility data in the temperature range 5.0~300 K were collected with an applied field of 500 Oe of a Quantum Design MPMS SQUID magnetometer.

1.2 Synthesis of the [Eu(DMSO)₃(H₂O)₃Cr(CN)₆]·H₂O

EuCl₃ (0.45 g, 1.75 mmol), DMSO (3.6 mL, 5.25 mmol) and K₃[Cr(CN)₆] (0.57 g, 1.75 mmol) reacted in the molar ratio of 1:3:1 in deionized water. Slow evaporation of the resultant, yellow mixture, in the dark at room temperature gave well-shaped single crystals [Eu(DMSO)₃(H₂O)₃Cr(CN)₆]·H₂O Anal. Calcd(%) for C₁₂H₂₆CrEuN₆O₇S₃ (666.53): C, 21.62; N, 12.61; H, 3.93. Found(%): C, 21.30; N, 12.42; H, 4.16.

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 α radiation (λ =0.071 073 nm) at 293 K. The sample selected for investigation has dimensions of 0.16 mm $\times$ 0.14 mm $\times$ 0.12 mm. A total of 14 540 independent reflections were measured to give 5 180 independent reflections (R_{int} =0.031 3). 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-square techniques (SHELXL-97) on F^2 . Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic 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 $w=1/[\sigma^2(F_o^2)+(0.000\ 9P)^2+0.95P]$ where $P=$

$(F_o^2+2F_c^2)/3$. The flack parameter of -0.003 4 is very close to zero, showing the absolute structure is correct. The crystal data and the experimental details for structural analyses are summarized in Table 1.

Table 1 Crystallographic data for the title complex

Empirical	C ₁₂ H ₂₆ CrEuN ₆ O ₇ S ₃
Formula	666.53
Temperature / K	293(2)
Wavelength / nm	0.071 073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
<i>a</i> / nm	0.972 2(3)
<i>b</i> / nm	1.489 5(4)
<i>c</i> / nm	1.748 6(5)
Volume / nm ³	2.532 0(12)
<i>Z</i>	4
Density / (Mg·m ⁻³)	1.748
$F(000)$	1 324
Crystal size / mm	0.16 $\times$ 0.14 $\times$ 0.12
Reflections collected	14 540
Independent reflections	5 180
Number of parameters	294
Goodness of fit on $F^2(s)$	1.085
Final R indices [$I>2\sigma(I)$]	$R_1=0.020\ 4$, $wR_2=0.043\ 4$
R indices (all data)	$R_1=0.023\ 4$, $wR_2=0.048\ 1$

CCDC: 272212.

2 Results and discussion

2.1 IR characterizations

The IR spectra of the complex shows three bonds at 2 131.1 cm⁻¹, 2 138.3 cm⁻¹, 2 146.4 cm⁻¹ in the range 2 000~2 200 cm⁻¹ that are attributed to CN⁻ stretching modes. The splitting suggests the presence of both bridged and nonbridged CN⁻ ligands. The strong bonds at 1 012.2 cm⁻¹, for the title complex are assigned to the S=O stretching vibration.

2.2 Crystal structure

Fig.1 shows the coordination environment of the Eu(III) in the complex and the packing diagram of the complex is given in Fig.2. The selected bond distances and angles are shown in Table 2. Table 3 gives the distances and angles related with the hydrogen bonding.

X-ray single-crystal structural analysis revealed that the title complex is made up of neutral cyanide-bridged Eu-Cr zigzag chains. One of DMSO molecules

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

Eu(1)-O(2)	0.232 8(2)	Eu(1)-N(4)#1	0.258 0(3)	N(1)-C(1)	0.115 2(5)
Eu(1)-O(3)	0.234 5(3)	Cr(1)-C(2)	0.207 3(4)	N(2)-C(2)	0.113 7(5)
Eu(1)-O(1)	0.235 5(2)	Cr(1)-C(3)	0.207 9(4)	N(3)-C(3)	0.115 1(4)
Eu(1)-O(6)	0.242 2(3)	Cr(1)-C(5)	0.208 0(4)	N(4)-C(4)	0.113 8(5)
Eu(1)-O(5)	0.243 1(3)	Cr(1)-C(1)	0.208 0(4)	N(4)-Eu(1)#2	0.258 0(3)
Eu(1)-O(4)	0.243 4(3)	Cr(1)-C(6)	0.208 1(4)	N(5)-C(5)	0.113 8(5)
Eu(1)-N(1)	0.257 1(3)	Cr(1)-C(4)	0.208 9(4)	N(6)-C(6)	0.114 0(5)
O(2)-Eu(1)-O(3)	143.55(10)	O(6)-Eu(1)-N(1)	144.79(10)	C(5)-Cr(1)-C(6)	87.28(15)
O(2)-Eu(1)-O(1)	141.42(10)	O(5)-Eu(1)-N(1)	72.77(10)	C(1)-Cr(1)-C(6)	170.83(16)
O(3)-Eu(1)-O(1)	74.23(10)	O(4)-Eu(1)-N(1)	72.04(10)	C(2)-Cr(1)-C(4)	174.69(16)
O(2)-Eu(1)-O(6)	80.15(10)	O(2)-Eu(1)-N(4)#1	81.30(10)	C(3)-Cr(1)-C(4)	87.77(17)
O(3)-Eu(1)-O(6)	73.53(10)	O(3)-Eu(1)-N(4)#1	111.68(11)	C(5)-Cr(1)-C(4)	92.77(15)
O(1)-Eu(1)-O(6)	116.41(11)	O(1)-Eu(1)-N(4)#1	73.60(11)	C(1)-Cr(1)-C(4)	95.22(16)
O(2)-Eu(1)-O(5)	73.70(9)	O(6)-Eu(1)-N(4)#1	69.89(10)	C(6)-Cr(1)-C(4)	91.09(16)
O(3)-Eu(1)-O(5)	76.16(10)	O(5)-Eu(1)-N(4)#1	141.44(10)	C(1)-N(1)-Eu(1)	147.9(3)
O(1)-Eu(1)-O(5)	141.49(10)	O(4)-Eu(1)-N(4)#1	79.44(11)	C(4)-N(4)-Eu(1)#2	174.4(3)
O(6)-Eu(1)-O(5)	77.17(10)	N(1)-Eu(1)-N(4)#1	144.25(12)	N(1)-C(1)-Cr(1)	168.8(3)
O(2)-Eu(1)-O(4)	70.27(10)	C(2)-Cr(1)-C(3)	86.93(17)	N(2)-C(2)-Cr(1)	175.7(4)
O(3)-Eu(1)-O(4)	143.80(10)	C(2)-Cr(1)-C(5)	92.54(16)	N(3)-C(3)-Cr(1)	177.3(3)
O(1)-Eu(1)-O(4)	76.58(10)	C(3)-Cr(1)-C(5)	179.22(14)	N(4)-C(4)-Cr(1)	176.5(4)
O(6)-Eu(1)-O(4)	140.08(10)	C(2)-Cr(1)-C(1)	85.10(15)	N(5)-C(5)-Cr(1)	178.8(4)
O(5)-Eu(1)-O(4)	117.35(11)	C(3)-Cr(1)-C(1)	94.73(15)	N(6)-C(6)-Cr(1)	176.4(4)
O(2)-Eu(1)-N(1)	107.91(11)	C(5)-Cr(1)-C(1)	85.79(15)	S(1')-O(1)-Eu(1)	156.0(5)
O(3)-Eu(1)-N(1)	81.77(11)	C(2)-Cr(1)-C(6)	89.24(16)	S(1)-O(1)-Eu(1)	142.50(18)
O(1)-Eu(1)-N(1)	79.09(11)	C(3)-Cr(1)-C(6)	92.15(15)		

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

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

D-H	A	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$\angle \text{DHA}$	$d(\text{D}\cdots\text{A})$
O4-H4A	N2 ⁱ	0.084 6	0.239 5	161.76	0.320 9
O4-H4B	N3 ⁱⁱ	0.085 1	0.217 0	136.19	0.284 6
O5-H5A	N6 ⁱⁱⁱ	0.084 2	0.204 9	177.31	0.289 1
O5-H5B	N5 ^{iv}	0.084 4	0.201 6	163.13	0.283 5
O6-H6A	N2 ^v	0.084 6	0.201 0	164.06	0.283 2
O6-H6B	O7 ⁱⁱ	0.084 4	0.198 3	164.65	0.280 6
O7-H7D	N6 ^{vi}	0.084 2	0.229 3	150.01	0.305 1
O7-H7E	N1 ⁱⁱⁱ	0.084 2	0.269 4	159.92	0.349 7

Symmetry transformations: ⁱ x, y, z ; ⁱⁱ $x-1/2, -y+3/2, -z+1$; ⁱⁱⁱ $-x+3/2, -y+1, z+1/2$; ^{iv} $-x+1, y+1/2, -z+3/2$;

^v $-x+1/2, -y+1, z+1/2$; ^{vi} $-x+1, y+1/2, -z+1/2$.

(S(1),C(7),C(8)) adopts statistic distribution. The asymmetric unit of the complex consists of one independent $[\text{Cr}(\text{CN})_6]^{3-}$ unit, one independent of Eu^{3+} unit, three DMSO and three water molecules. The Eu atoms are eight-coordinate: two nitrogen atoms of cyanide bridge and six oxygen atoms of three DMSO and three water

molecules. Six cyanide carbon atoms around the Cr centers build slightly distorted octahedral geometries. The bridging cyano ligands coordinate to the Eu(III) ion ($\text{Eu}(1)-\text{N}(1)=0.257\ 1(3)$ nm and $\text{Eu}(1)-\text{N}(4)\#1=0.258\ 0(3)$ nm) in a bent fashion, with bond angles of $147.9(3)^\circ$ for $\text{C}(1)-\text{N}(1)-\text{Eu}(1)$ and $174.4(3)^\circ$ for $\text{C}(4)-$

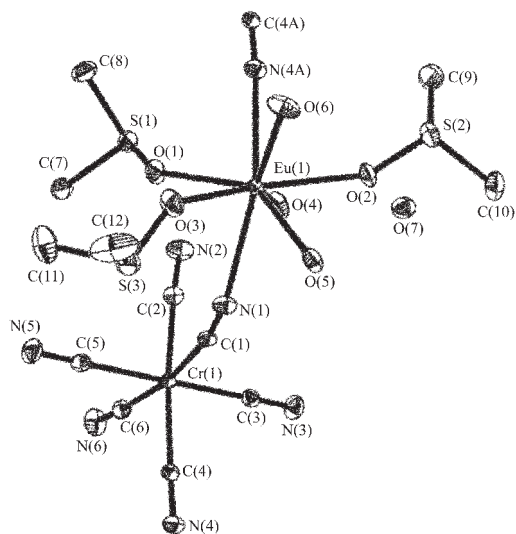


Fig.1 Molecular structure of the title complex

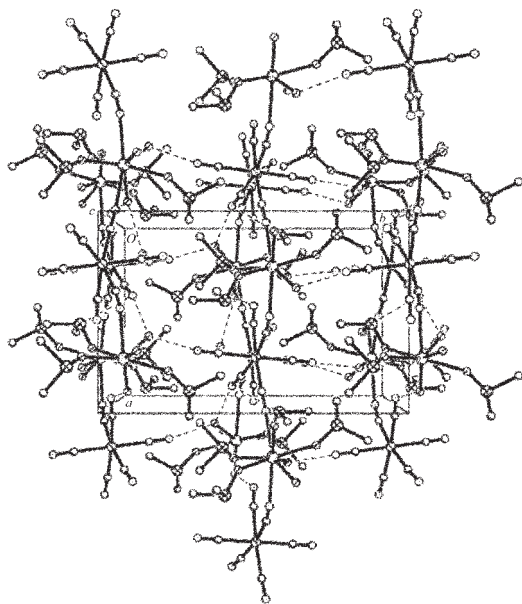


Fig.2 Packing of the title complex

N(4)-Eu(1)#2. (Where #1 denotes the symmetry transformations $x-1, y, z$ and #2 denotes $x+1, y, z$). The Eu-O bond distances range from 0.232 8(2) to 0.243 4(3) nm. The Cr-C bond distances and most of the N-C-Cr bond angles are in the normal range, but the N-C-Cr bonds that are involved in bridging exhibit depart somewhat from strict linearity ($168.8(3)^\circ$ and $176.5(4)^\circ$). The terminal cyanide ligands are hydrogen-bonded to the water molecules, with the $O \cdots N$ separations ranging from 0.280 6 to 0.349 7 nm. Therefore, the molecular structure is a hydrogen-bonded 3D network derived from EuCr chains.

2.3 Magnetic properties

The variable-temperature (5~300 K) magnetic susceptibilities of the title complex has been measured on a crystalline sample in a field of 500 Oe. A plot of $\chi_m T$ vs T for the complex is shown in Fig.3, where χ_m is the magnetic susceptibility per EuCr unit.

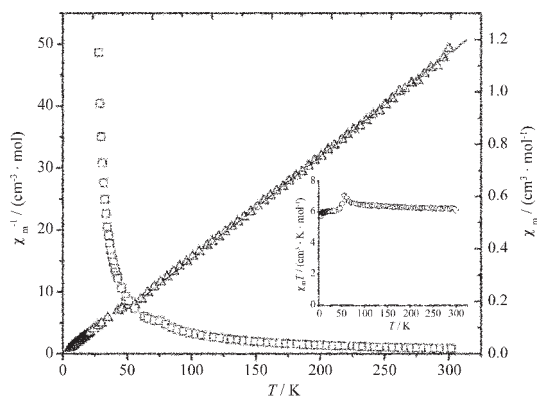


Fig.3 Temperature dependence of magnetic susceptibility per EuCr unit measured at 500 Oe
Inset: $\chi_m T$ vs T .

From the plot of χ_m vs T for the complex, it is very clearly that the magnetic susceptibility obeys the Curie-Weiss law with a positive Weiss constant, θ , of 1.28 K. This reveals that the Eu(III)-Cr(III) ferromagnetic coupling is comparatively weak. The Curie constant, C , is equal to $6.22 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, close to the expected value $7.875 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ with $g=2.0$. From Fig.3, we can see the $\chi_m T$ value at 300 K is *ca.* $6.09 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, which keeps almost constantly with decreasing temperature, reaching a maximum value of $7.05 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 56 K. With a further decrease in temperature, $\chi_m T$ decreases, reaching a minimum value of $5.75 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 5 K. Such magnetic behaviour is characteristic of dominant ferromagnetic interactions upon which weak antiferromagnetic interactions are superimposed^[27].

References:

- [1] Zhang S W, Fu D G, Sun B Y, et al. *Inorg. Chem.*, **2000**,**39**: 1142~1146
- [2] Ferlay S, Mallah T, Vaissermann J, et al. *Chem. Commun.*, **1996**:2481~2482
- [3] Smith J A, Galan-Mascaros J R, Clerac R, et al. *Chem. Commun.*, **2000**:1077~1078
- [4] Langenberg K V, Batten S R, Berry K J, et al. *Inorg. Chem.*, **1997**,**36**:5006~5015

- [5] Holmes S M, Girolami G S. *J. Am. Chem. Soc.*, **1999**,**121**: 5593~5594
- [6] Kou H Z, Gao S, Ma B Q, et al. *Chem. Commun.*, **2000**:713~714
- [7] Sra A K, Andruh M, Kahn O, et al. *Angew. Chem.*, **1999**,**38**: 2606~2609
- [8] Kou H Z, Gao S, Bu W M, et al. *Dalton Trans.*, **1999**:2477~2480
- [9] Ohbas M, Usuki N, Fukita N, et al. *Angew. Chem.*, **1999**,**38**: 1795~1798
- [10] Mondal N, Saha M K, Bag B, et al. *Dalton Trans.*, **2000**: 1601~1604
- [11](a)Verdaguer M. *Science*, **1996**,**272**:698~699
(b)Sato O, Iyoda T, Fujishima A, et al. *Science*, **1996**,**272**: 704~705
- [12]Marvillers A, Parsons S, Riviere E, et al. *Chem. Commun.*, **1999**:2217~2218
- [13]Miller J S, Epstein A J. *Angew. Chem.*, **1994**,**33**:385~415
- [14]Stumpf H O, Ouahab L, Pel Y, et al. *J. Am. Chem. Soc.*, **1994**, **116**:3866~3874
- [15]Holmes S M, Girolami G. *J. Am. Chem. Soc.*, **1999**,**121**:5593~5594
- [16]Olivier K. *Nature*, **1995**,**378**:667~668
- [17]Hatlevik O, Buschmann W E, Zhang J, et al. *Adv. Mater.*, **1999**,**11**:914~918
- [18]Kahn O. *Angew. Chem.*, **1985**,**24**:834~850
- [19]Hulliger F, Landolt M, Vetsch H. *J. Solid State Chem.*, **1976**, **18**:283~291
- [20](a)Garcia-Granda S, Morales A D, Ruiz E R, et al. *Acta Crystallogr.*, **1996**,**C52**:1679~1681
(b)Yi T, Gao S, Chen, X W. *Acta Crystallogr.*, **1998**,**C54**: 41~43
- [21]Kautz J A, Mullica D F, Cunningham B P, et al. *J. Mol. Struct.*, **2000**,**523**:175~182
- [22]Mullica D F, Farmer J M, Cunningham B P, et al. *J. Coord. Chem.*, **2000**,**49**:239~240
- [23]Kou H Z, Yang G M, Liao D Z, et al. *J. Chem. Crystallogr.*, **1998**,**28**:303~305
- [24]Kou H Z, Gao S, Sun B W, et al. *Chemistry of Materials. Communications*, **2001**,**13**:1431~1433
- [25]Kou H Z, Gao S, Jin X L. *Inorg. Chem.*, **2001**,**40**:6295~6300
- [26]Michaut C, Ouahab L, Bergerat P, et al. *J. Am. Chem. Soc.*, **1996**,**113**:3610~3611