

Note

Assembly of a New Cyano-bridged 4f-3d Dimer $\text{Sm}(\text{DMSO})_4(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_6$ and Crystal Structure of $[\text{K}_3(18\text{-crown-6})_3(\text{H}_2\text{O})_4]\text{Cr}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$

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A new cyano-bridged binuclear 4f-3d complex $\text{Sm}(\text{DMSO})_4(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_6$ was synthesized and characterized by single crystal structure analysis. It crystallizes in monoclinic, space group $P2_1$ with $a = 0.9367(2)$ nm, $b = 1.3917(3)$ nm, $c = 1.1212(2)$ nm, $\beta = 99.88(3)^\circ$ and $Z = 2$. In this binuclear complex, Sm atom is eight coordinated and linked to the Cr atom by a cyano bridge. The molecules packs to form 3D structure due to the hydrogen bonds among them. $[\text{K}_3(18\text{-C-6})_3(\text{H}_2\text{O})_4]\text{Cr}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (18-C-6 represents 18-crown-6-ether) that was synthesized as a byproduct in the preparation of a Gd—Cr complex is also structurally characterized. Crystal data: triclinic, space group $P-1$ with $a = 1.0496(7)$ nm, $b = 1.1567(14)$ nm, $c = 1.3530(13)$ nm, $\alpha = 94.15(9)^\circ$, $\beta = 96.04(8)^\circ$, $\gamma = 95.25(9)^\circ$ and $Z = 1$. $[\text{K}_3(18\text{-C-6})_3(\text{H}_2\text{O})_4]\text{Cr}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ consists of ionic $[\text{K}_3(18\text{-C-6})_3(\text{H}_2\text{O})_4]^{3+}$ and $[\text{Cr}(\text{CN})_6]^{3-}$ pairs, of which the $[\text{K}_3(18\text{-C-6})_3(\text{H}_2\text{O})_4]^{3+}$ ion is a trinuclear cluster connected by water, and K atoms are eight coordinated by eight oxygen atoms of one 18-C-6 and two water molecules.

Keywords cyano-bridged complex, crystal structure, binuclear, lanthanide hexacyanometallate, crown ether

Introduction

Considerable interests in cyano-bridged Prussian blue analogues that show rich structures and interesting magnetic properties have increased in the last decades. An attractive area in these studies is to prepare cyano-bridged bimetallic lanthanide-transition metal complexes, which are potential catalytic, semiconductive and magnetic materials. A series of these complexes, such as $[\text{Ln}(\text{DMF})_l(\text{H}_2\text{O})_m\text{M}(\text{CN})_6] \cdot \text{H}_2\text{O}$ ($l = 2$ or 4 , $\text{M} = \text{Fe}$, Cr , Mn), with polynuclear $\sim 2\text{D}$ structures has been synthesized and subjected to single crystal structure analyses.^{1-3,7} The use of DMSO as a ligand for construction of lanthanide hexacyanometallate⁴ has rarely been reported because of the difficulty in preparing single crystals. Herein we report the structures of a new binuclear complex, $\text{Sm}(\text{DMSO})_4(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_6$ (1), and an ionic pair com-

plex, $[\text{K}_3(18\text{-crown-6})_3(\text{H}_2\text{O})_4]\text{Cr}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (2), which was unexpectedly obtained during our attempt to prepare the Gd—Cr analog of 1.

Experimental

Syntheses

All of the chemicals and solvents used in the synthesis were of reagent grade. The precursors $\text{K}_3[\text{Cr}(\text{CN})_6]$ and $[\text{Sm}(\text{pyr})_4(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ (pyr = 2-pyrrolidone) were prepared by the reported method.^{5,6}

$\text{Sm}(\text{DMSO})_4(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_6$

Slow diffusion of ethanol to a DMSO solution of $[\text{Sm}(\text{pyr})_4(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ for several weeks led to yellow crystals suitable for X-ray diffraction analysis.

$[\text{K}_3(18\text{-crown-6})_3(\text{H}_2\text{O})_4]\text{Cr}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$

To an absolute ethanol solution of $\text{K}_3\text{Cr}(\text{CN})_6$ (0.1 mmol) and 18-Crown-6 (0.3 mmol) was added $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (0.1 mmol) in DMSO (2 mL). Slow evaporation of the solution at room temperature produced yellow crystals.

Crystallographic data collection and structure determination

Data collections of single crystals 1 and 2 were carried out at 293 K on a Bruker Smart CCD and on a Bruker Siemens P4 diffractometer with highly oriented graphite crystal $\text{Mo K}\alpha$ radiation ($\lambda = 0.071073$ nm). The structures were solved by the direct method (SHELXS-97) and refined by full matrix least-squares (SHELXL-97) on F^2 . Anisotropic thermal parameters were used on all non-hydrogen atoms. Hydro-

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gen atoms were added geometrically and refined using a riding model. Intensity data were corrected for Lp effects and empirical absorption correction. Three of the sulfur atoms of the DMSO in **1** experience serious disorder, therefore a split-atom model was applied. The crystal data are summarized in Table 1.

Results and discussion

Syntheses

Failing to obtain crystals of complex **1** by slowly evaporating the mixture of $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, DMSO and $\text{K}_3\text{Cr}(\text{CN})_6$ in the ratio of 1:4:1 (molar ratio) in water, we tried slow diffusion of ethanol vapor into the DMSO solution of $[\text{Sm}(\text{pyr})_4(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ and finally got crystals suitable for single crystal analysis. It involves the substitution of DMSO for pyr. It is supposed that the molar ratio of the lanthanide to the organic ligand can determine the structure of the resulting complex. For example, the complexes with Ln/ligand = 1:2 (molar ratio) lead to 2D structures, while polynuclear and 1D arrays are observed in complexes with Ln/ligand = 1:4 (molar ratio).⁷ It has been found that $\text{SmFe}(\text{CN})_6(\text{DMSO})_2 \cdot \text{H}_2\text{O}$ has 2D structure.⁴ So the ratio of Sm/DMSO = 1:4 (molar ratio) in complex **1** results in low-dimensional Sm—Cr complex.

Considering that the polar solvent, water, is unfavourable to form the extended network structure, we tried to obtain a 2D or 3D Gd—Cr complex by using ethanol as the solvent instead of water. Unexpectedly, we got the single

crystals of $[\text{K}_3(18\text{-crown-6})_3(\text{H}_2\text{O})_4]\text{Cr}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ instead of the Gd—Cr complex.

Crystal structures

ORTEP drawings of crystal structures for complexes **1** and **2** are shown in Figs. 1 and 3, respectively. Figs. 2 and 4 are the unit packing diagrams of complexes **1** and **2**, respectively. The selected bond lengths and angles are listed in Table 2, respectively.

The structure of **1** consists of a dimer connected by a cyano-bridge. The eight coordination positions of the Sm atom are occupied by the N atom [N(1)] from the bridging cyanide, three O atoms [O(5), O(6), O(7)] from water and four O atoms [O(1), O(2), O(3), O(4)] of four DMSO molecules. The bond lengths of Sm—O_{DMSO} range from 0.2380(6) nm to 0.2427(5) nm, which are a little shorter than those of Sm—O_{water} [0.2427(5)—0.2519(5) nm] and similar to those of Sm—O_{DMSO} in some mononuclear species.^{8,9} The bridging cyanide coordinates to the Sm atom with the distance of N(1)—Sm(1) [0.2599(6) nm] which is longer than the bond lengths of Sm—N_{cyano} (0.2452—0.2504 nm) in the cyano-bridged Sm—Fe species,^{1,4} and with the angle of C(1)—N(1)—Sm(1) [168.3(6)°] which is similar to those in the Sm—Fe species.^{1,4} The distance of adjacent Sm···Cr [0.5797(2) nm] is a little longer than that of Sm···Fe (0.5514 and 0.5588 nm) in $\text{SmFe}(\text{CN})_6(\text{DMSO})_2 \cdot \text{H}_2\text{O}$.⁴

Table 1 Crystal data for complexes **1** and **2**

	1	2
Formula	$\text{C}_{14}\text{H}_{30}\text{CrN}_6\text{O}_7\text{S}_4\text{Sm}$	$\text{C}_{42}\text{H}_{92}\text{CrK}_3\text{N}_6\text{O}_{28}$
Formula weight	725.03	1298.52
Temperature	293(2) K	293(2) K
Wavelength	0.071073 nm	0.071073 nm
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$	$P-1$
Unit cell dimensions	$a = 0.9367(2)$ nm $b = 1.3917(3)$ nm $c = 1.1212(2)$ nm $\beta = 99.88(3)^\circ$	$a = 1.0496(7)$ nm $b = 1.1567(14)$ nm $c = 1.3530(13)$ nm $\alpha = 94.15(9)^\circ$ $\beta = 96.04(8)^\circ$ $\gamma = 95.25(9)^\circ$
Volume	1.4399(5) nm ³	1.621(3) nm ³
Z	2	1
Calculated density	1.672 Mg/m ³	1.330 Mg/m ³
Absorption coefficient	2.727 mm ⁻¹	0.450 mm ⁻¹
$F(000)$	724	691
Reflections collected	6026	5884
Independent reflections	3844	5577
Reflections with $I > 2\sigma(I)$	3559	2917
Data/restraints/params	3844/1/326	5577/0/364
Goodness-of-fit on F^2	1.061	1.223
$R_1[I > 2\sigma(I)]$	0.0338	0.1104
$wR_2(\text{all data})$	0.0876	0.3730
Largest diff. peak	898 e/nm ³	769 e/nm ³
Largest diff. hole	-503 e/nm ³	-749 e/nm ³

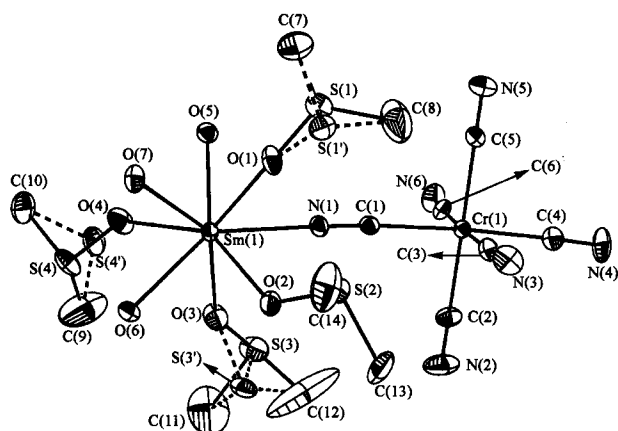


Fig. 1 Molecular structure of 1.

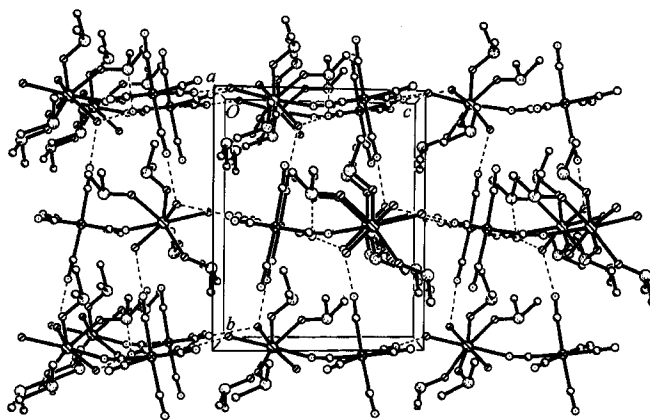


Fig. 2 Unit cell packing diagram of 1, showing the hydrogen bonds.

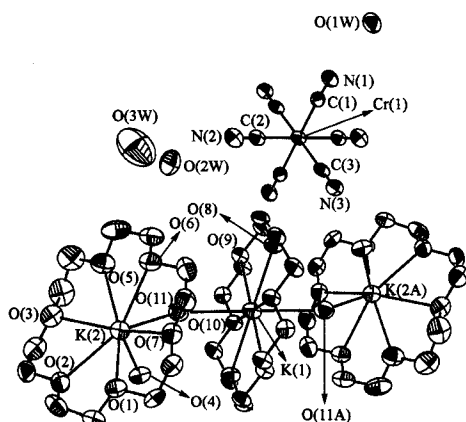


Fig. 3 Molecular structure of 2.

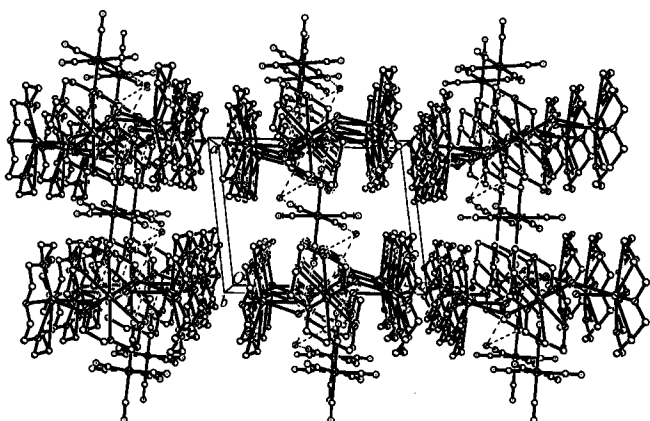


Fig. 4 Unit cell packing diagram of 2, showing the hydrogen bonds.

Table 2 Bond lengths (nm) and angles ($^{\circ}$) of 1 and 2

Bond lengths (nm) and bond angles ($^{\circ}$) of 1					
Sm(1)—O(1)	0.2383(6)	Sm(1)—O(6)	0.2519(5)	Cr(1)—C(3)	0.2068(9)
Sm(1)—O(2)	0.2380(6)	Sm(1)—O(7)	0.2427(5)	Cr(1)—C(4)	0.2096(8)
Sm(1)—O(3)	0.2413(6)	Sm(1)—N(1)	0.2599(6)	Cr(1)—C(5)	0.2089(7)
Sm(1)—O(4)	0.2400(6)	Cr(1)—C(1)	0.2098(8)	Cr(1)—C(6)	0.2082(9)
Sm(1)—O(5)	0.2458(6)	Cr(1)—C(2)	0.2065(8)	Cr(1)⋯Sm(1)	0.5797(2)
O(2)—Sm(1)—O(1)	76.2(2)	O(5)—Sm(1)—N(1)	77.6(2)		
O(2)—Sm(1)—O(4)	145.5(2)	O(6)—Sm(1)—N(1)	140.81(18)		
O(2)—Sm(1)—O(3)	82.1(3)	N(5)—C(5)—Cr(1)	178.3(11)		
O(1)—Sm(1)—O(3)	145.0(2)	N(3)—C(3)—Cr(1)	176.2(8)		
O(4)—Sm(1)—O(3)	76.2(3)	N(1)—C(1)—Cr(1)	174.4(7)		
O(2)—Sm(1)—N(1)	78.9(2)	C(1)—N(1)—Sm(1)	168.3(6)		
O(1)—Sm(1)—N(1)	74.4(2)	N(4)—C(4)—Cr(1)	176.6(10)		
O(4)—Sm(1)—N(1)	119.6(2)	N(2)—C(2)—Cr(1)	178.1(9)		
O(3)—Sm(1)—N(1)	74.7(2)	N(6)—C(6)—Cr(1)	177.6(9)		
O(7)—Sm(1)—N(1)	144.0(2)				

Continued

Bond lengths (nm) and bond angles (°) of 2					
K(2)—O(5)	0.2766(8)	K(2)—O(3)	0.2878(8)	K(1)—O(8)	0.2753(6)
K(2)—O(7)	0.2819(7)	K(2)—O(2)	0.2877(7)	K(1)—O(10)	0.2797(5)
K(2)—O(4)	0.2822(6)	K(2)—O(6)	0.2976(7)	K(1)—O(11)	0.2860(7)
K(2)—O(1)	0.2865(7)	K(2)—O(11)	0.2989(7)	K(1)—O(9)	0.2874(5)
C(1)-Cr(1)-C(3)		88.7(3)	N(2)-C(2)-Cr(1)		179.2(7)
C(1)-Cr(1)-C(2)		89.6(3)	N(3)-C(3)-Cr(1)		177.6(7)
C(3)-Cr(1)-C(2)		89.6(3)	O(4)-K(2)-O(11)		58.59(19)
N(1)-C(1)-Cr(1)		176.8(7)			

The $\text{Cr}(\text{CN})_6$ moiety of complex **1** is nearly octahedral with the C—Cr bond lengths ranging from 0.2065(8) nm to 0.2098(8) nm. The Cr—C—N bonds are almost linear [$174.4(7)^\circ$ — $178.3(11)^\circ$].

The five unbridging cyano nitrogen atoms are H-bonded to the coordinated water molecules of five adjacent $\text{Sm}(\text{DM-SO})_4(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_6$ molecules giving rise to a three-dimensional network (N···O separations: 0.2786—0.2984 nm).

The structure of **2** consists of ionic $[\text{K}_3(18\text{-C-6})_3(\text{H}_2\text{O})_4]^{3+}$ and $[\text{Cr}(\text{CN})_6]^{3-}$ pairs. In $[\text{K}_3(18\text{-C-6})_3(\text{H}_2\text{O})_4]^{3+}$, K atoms lies in the 18-crown-6 rings. Each K^+ ion is eight coordinated by six O atoms of crown ether and two of water, whereas two coordinated O water atoms link the three K^+ cations leading to a novel trinuclear cationic cluster. The K^+ ion in the middle exhibits the *trans* configuration and is within the least-squares plane of the coordinated 18-crown-6, while the terminal K^+ ions are in a *cis* configuration with the *cis* $\text{O}_w\text{-K-O}'_w$ bond angle of $58.59(19)^\circ$. The K—O_{18-C-6} bond lengths range from 0.2753 to 0.2976 nm, which are similar to that in complex $[\text{K}(18\text{-C-6})_2[\text{Cd}(\text{mnt})_2]^{10}$.

The $[\text{K}_3(18\text{-C-6})_3(\text{H}_2\text{O})_4]^{3+}$ and $[\text{Cr}(\text{CN})_6]^{3-}$ units formed two separate layers, which linked by hydrogen bonds involving free water molecules between them and arranged alternatively to form a three-dimensional geometry.

References

- 1 Kou, H. Z.; Yang, G. M.; Liao, D. Z.; Cheng, P.; Jiang, Z. H.; Yan, S. P.; Huang, X. Y.; Wang, G. L. *J. Chem. Crystallogr.* **1998**, *28*, 303.
- 2 Yan, B.; Chen, Z. D.; Wang, S. X.; Gao, S. *Chem. Lett.* **2001**, 350.
- 3 Kou, H. Z.; Gao, S.; Sun, B. W.; Zhang, J. *Chem. Mater.* **2001**, *13*, 1431.
- 4 Yang, C.; Guo, G. C.; Ma, H. W.; Liu, J. C.; Zhang, X.; Zheng, F. K.; Lin, S. H.; Zhou, G. W.; Mao, J. G.; Huang, J. S. *Chin. J. Struct. Chem.* **2001**, *20*, 229 (in Chinese).
- 5 Cruser, F. V. D.; Miller, E. H. *J. Am. Chem. Soc.* **1906**, *25*, 245.
- 6 Kou, H. Z.; Gao, S.; Jin, X. *J. Rare Earths* **2002**, *20*, 363.
- 7 Kou, H. Z.; Gao, S.; Jin, X. L. *Inorg. Chem.* **2001**, *40*, 6295.
- 8 Semenova, L. I.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1996**, *49*, 997.
- 9 Xiong, R. G.; Zuo, J. L.; You, X. Z. *Polyhedron* **1996**, *15*, 3321.
- 10 Wang, D. Q.; Yu, Q. J.; Dou, J. M. *Chin. J. Chem.* **2002**, *20*, 191.

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