



Syntheses, structures and magnetic properties of cyano-bridged Sm(III)M(V) (M = Mo, W) assemblies with zigzag chains

Xiao-Zhen Yang^a, Hu Zhou^a, Su-Yan Qian^a, Ai-Hua Yuan^{b,*}, Hong-Bo Zhou^c, You Song^{d,**}

^a School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China

^b School of Biology and Chemistry Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China

^c School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China

^d State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

ARTICLE INFO

Article history:

Received 18 June 2012

Accepted 24 July 2012

Available online 29 July 2012

Keywords:

Octacyanometalate

Lanthanide

Zigzag chain

Magnetic properties

ABSTRACT

The reaction of Sm³⁺ ion with [M(CN)₈]³⁻ (M = W, Mo) units in the presence of the chelated ligand phen has isolated two octacyanometalate-based assemblies [Sm(phen)(DMF)₅][M(CN)₈]·CH₃OH·H₂O (M = Mo, **1**; W, **2**). Single crystal X-ray diffraction analysis revealed that both compounds are isostructural and the structure consists of Sm³⁺ centers and [M(CN)₈]³⁻ units linked alternatively to generate a one-dimensional (1D) zigzag chain. The chains are further connected together through hydrogen-bonding and π-π stack interactions to form a 3D supra-molecular network. The magnetic results revealed that the ferromagnetic interactions were observed between Sm(III) and M(V) centers in both compounds.

© 2012 Elsevier B.V. All rights reserved.

Cyano-bridged metal assemblies have been focused on the design and synthesis of new molecule-based magnets from the viewpoint of potential utility for functional materials [1–5]. Recently, octacyanometalates [M(CN)₈]^{3-/4-} (M = Mo, W) have received increasing attention owing to their flexible coordination modes [6]. On the other hand, the coordination geometries of lanthanide ions are difficult to control because of their lability and the absence of design strategies. Thus, it will be challenging to synthesize octacyanometalate-based lanthanide assemblies with specific topologies and therefore magnetic properties. However, recent studies indicated that the chelated ligands were employed to control the number and spatial arrangement of coordination positions available on metal centers for CN-bridging, hence generating low-dimensional architectures rather than extended networks [7,8]. Our group has applied this building strategy in the preparation of cyano-bridged 4f-3d/4d/5d helical chains [9,10]. As a part of a detailed study of cyano-bridged assemblies, above success inspires us to further construct magnetic systems with low-dimensionality and unique magnetisms.

In this contribution, we presented the syntheses, crystal structures and magnetic properties of two isostructural octacyanometalate-based lanthanide compounds [Sm(phen)(DMF)₅][M(CN)₈]·CH₃OH·H₂O (M = Mo, **1**; W, **2**) with 1D zigzag chain by the self-assembly of [M(CN)₈]³⁻ units and Sm³⁺ ion in the presence of the chelated ligand phen.

Single crystals of both compounds were prepared by combining a CH₃OH solution of Sm(NO₃)₃·6H₂O (0.05 mmol) and phen (0.15 mmol) with a CH₃OH/DMF (V/V = 3/1) solution of [HN(*n*-C₄H₉)₃]₃[M(CN)₈]·4H₂O (M = Mo, W) [**11**] (0.05 mmol) by the slow diffusion method at room temperature in the dark. After about two weeks, orange block-shaped crystals were obtained. IR (KBr), ν_{C≡N} for compound **1**: 2172, 2144, 2114 cm⁻¹; ν_{C≡N} for compound **2**: 2171, 2145, 2109 cm⁻¹.

Single crystal X-ray diffraction analysis revealed that compounds **1** and **2** are isostructural and crystallize in the monoclinic system with space group P2₁/c [12]. Here only the structure of compound **1** was described in detail (Fig. 1). The asymmetric unit of compound **1** consists of one [Sm(phen)(DMF)₅]³⁺ cation, one [Mo(CN)₈]³⁻ anion, one crystallized CH₃OH and H₂O molecules. The eight-coordinated [Mo(CN)₈]³⁻ unit adopts a slightly distorted square antiprism, where two CN groups are bridged to adjacent Sm atoms and the others are terminal. The metric parameters of the [Mo(CN)₈]³⁻ unit are typical for octacyanometalates [13–15]. The Mo1-C bond distances range from 2.155 to 2.175 Å, and the Mo1-CN angles remain almost linear with the maximum deviation from linearity of 3.6° (Supplementary material, Table S1). The Sm center exhibits a nine-coordinated environment with two cyano-nitrogen atoms, two nitrogen atoms from one phen ligand, and five oxygen atoms from five DMF molecules. The coordination geometry around the Sm atom is a tricapped trigonal prismatic with the capping positions occupied by N1, N6¹ and N10 atoms (symmetry code: (i) x, -y + 1/2, z + 1/2). The average Sm1-N and Sm1-O bond lengths are 2.627 and 2.418 Å, respectively. Due to the large ionic radii of the lanthanide ions, the cyanide bridges are exceptionally long and the Sm1-NC bonds are bent (164.4–176.1°), opposition to the linear Mo1-CN units. The geometrical data of the Sm(III) center conform to those reported for

*Corresponding author. Tel./fax: +86 51185638920.

**Corresponding author. Tel.: +86 2583593739; fax: +86 2583314502.

E-mail addresses: aihuyuan@163.com (A.-H. Yuan), yousong@nju.edu.cn (Y. Song).

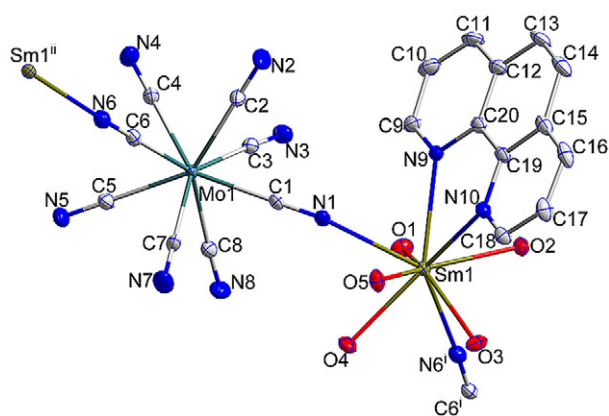


Fig. 1. ORTEP diagram of compound **1**, showing the 30% probability thermal motion ellipsoid. All hydrogen atoms, crystallized CH₃OH and H₂O molecules, and carbon and nitrogen atoms of coordinated DMF molecules have been omitted for clarity. Symmetry codes: (i) $x, -y + 1/2, z + 1/2$; (ii) $x, -y + 1/2, z - 1/2$.

the compounds [Pr(tmphen)(DMF)₅][M(CN)₈]·DMF·2H₂O (M = Mo, W) [10].

As a result, the Sm³⁺ ions and [Mo(CN)₈]³⁻ units are linked in an alternating fashion, generating 1D 2,2-zigzag chains running parallel to the crystallographic 2₁ axis, which are separated by the DMF molecules and phen ligands (Fig. 2). The nearest interchain distances for Mo1···Mo1 and Mo1···Sm1 are about 9.862 and 5.801 Å, respectively. Two terminal cyano ligands and one crystallized H₂O molecule are involved in the hydrogen bonding network. Thus, the {Sm^{III}Mo^V} chains interact through hydrogen-bonding (O7–H7X···N5, O7–H7Y···N7^{iv}, symmetry code: (iv) $-x + 1, -y, -z$) and π – π stacking interactions (face–face distance of 3.433 Å) between two adjacent interchain aromatic rings of phen from neighboring chains, forming a 3D supramolecular network.

The temperature-dependent magnetic susceptibilities of both compounds were investigated in the temperature range of 1.8–300 K in a field of 100 Oe (Fig. 3). The $\chi_M T$ values at 300 K are 0.57(1) and 0.55(2) cm³ K mol⁻¹, which are higher than the expected value (0.46 cm³ K mol⁻¹) calculated on the basis of the free ion approximation taking only the ⁶H_{5/2} ground state into consideration ($J = 5/2$, $g_J = 2/7$ for Sm(III), and $S = 1/2, g = 2$ for M(V)) [16]. The disagreement can be attributed to the presence of thermally populated excited states, which is well-known for cyanide-based Sm(III) compounds [17–24]. On cooling the temperatures, the $\chi_M T$ values decrease to reach the minimum 0.47(1) at 15 K and 0.46(2) cm³ K mol⁻¹ at 10 K. Obviously, the nature of the magnetic coupling between Sm(III) and M(V) ions cannot simply be determined from the decrease of $\chi_M T$, which should be due to the superposition of thermal depopulation of the low-lying excited states of Sm(III) and the Sm(III)–M(V) magnetic interaction. With a further decrease of temperatures, the $\chi_M T$ values sharply increase to 0.63(1) and 0.58(2) cm³ K mol⁻¹ at 1.8 K, suggesting a ferromagnetic character, which can be ascribed to the ferromagnetically

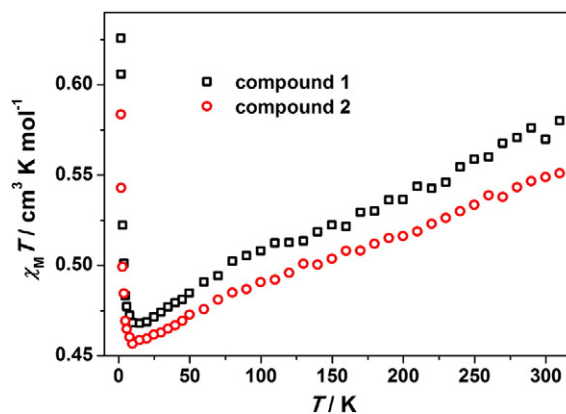


Fig. 3. Temperature dependence of $\chi_M T$ for compounds **1** and **2**.

coupled Sm(III) and M(V) spins overcoming the depopulation of the Stark levels of Sm(III) ion.

The field dependence of the magnetization and ac susceptibility was performed to get more insight in the type of magnetic interactions. The magnetization (Fig. 4) of both compounds increases monotonically as the magnetic field increases and reach the unsaturated values of 1.24(1) and 1.21(2) $N\mu_B$ at 70 kOe, which are higher than those (0.9–1.1 $N\mu_B$) observed in other octacyanometalate-based Sm(III) compounds with ferromagnetic interactions [5,19,21,22,25]. So the magnetic interactions between Sm(III) and M(V) ions in our case are also ferromagnetic. The χ' component of ac susceptibility increased monotonically as temperature decreased and no signal was observed in the χ'' component, suggesting the absence of the long-range magnetic ordering for both compounds at low temperatures (Fig. S1).

In summary, two isostructural octacyanometalate-based Sm(III) M(V) (M = Mo, W) zigzag chains have been prepared and characterized structurally and magnetically. The ferromagnetic interactions were found between Sm(III) and M(V) ions through cyanide bridges. The building block strategy presented here indicated that the aromatic chelated ligands were crucial to construct low-dimensional systems rather than extended networks. Further work along this line is in progress in our laboratory.

Acknowledgments

This research was supported by the projects of National Natural Science Foundation (Nos. 51072072, 51102119) and Natural Science Foundation of Jiangsu Province (Nos. BK2010343, BK2011518).

Appendix A. Supplementary data

CCDC numbers: 884439(1) and 884440(2) contains the supplementary crystallographic data for compounds **1** and **2**. This data can

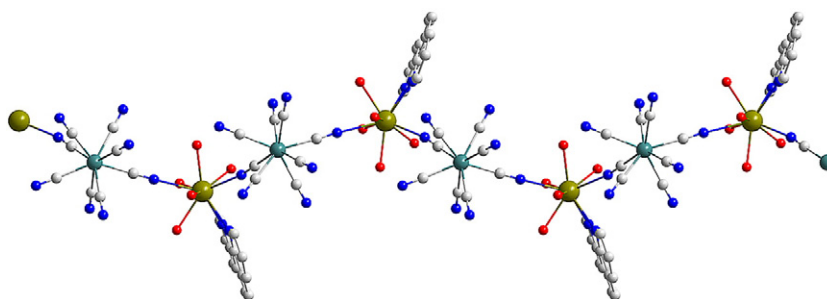


Fig. 2. Perspective view of 1D zigzag chain for compound **1**.

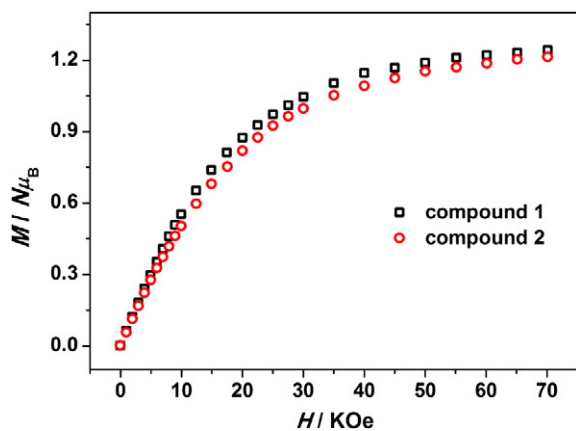


Fig. 4. Field dependence of the magnetization performed at 1.8 K for compounds **1** and **2**.

be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths (Å) and angles (°) for compounds **1** and **2**. Temperature dependence of the ac susceptibility for compounds **1** and **2**. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.inoche.2012.07.047>.

References

- [1] C. Bartual-Murgui, L. Salmon, A. Akou, N.A. Ortega-Villar, H.J. Shepherd, M. Carmen Muñoz, G. Molnár, J.A. Real, A. Bousseksou, Synergetic effect of host-guest chemistry and spin crossover in 3D Hofmann-like metal-organic frameworks [Fe(bpac)M(CN)₄] (M = Pt, Pd, Ni), *Chem. Eur. J.* 18 (2012) 507–516.
- [2] S. Ohkoshi, K. Imoto, Y. Tsunobuchi, S. Takano, H. Tokoro, Light-induced spin-crossover magnet, *Nat. Chem.* 3 (2011) 564–569.
- [3] A.E. Phillips, G.J. Halder, K.W. Chapman, A.L. Goodwin, C.J. Kepert, Zero thermal expansion in a flexible, stable framework: tetramethylammonium copper(I) zinc(II) cyanide, *J. Am. Chem. Soc.* 132 (2010) 10–11.
- [4] J. Larionova, Y. Guari, C. Sangregorio, C. Guérin, Cyano-bridged coordination polymer nanoparticles, *New J. Chem.* 33 (2009) 1177–1190.
- [5] E. Chelebaeva, J. Larionova, Y. Guari, R.A.S. Ferreira, L.D. Carlos, F.A.A. Paz, A. Trifonov, C. Guérin, Luminescent and magnetic cyano-bridged coordination polymers containing 4d–4f ions: toward multifunctional materials, *Inorg. Chem.* 48 (2009) 5983–5995.
- [6] B. Sieklucka, R. Podgajny, T. Korzeniak, B. Nowicka, D. Pinkowicz, M. Kozieł, A decade of octacyanides in polynuclear molecular materials, *Eur. J. Inorg. Chem.* (2011) 305–326.
- [7] H.-H. Zhao, N. Lopez, A. Prosvirin, H.T. Chifotides, K.R. Dunbar, Lanthanide-3d cyanometalate chains Ln(III)-M(III) (Ln = Pr, Nd, Sm, Eu, Gd, Tb; M = Fe) with the tridentate ligand 2,4,6-tri(2-pyridyl)-1,3,5-triazine (tptz): evidence of ferromagnetic interactions for the Sm(III)-M(III) compounds (M = Fe, Cr), *Dalton Trans.* (2007) 878–888.
- [8] X.-M. Chen, G.-F. Liu, Double-stranded helices and molecular zippers assembled from single-stranded coordination polymers directed by supramolecular interactions, *Chem. Eur. J.* 8 (2002) 4811–4817.
- [9] D.-Y. Yu, L. Li, H. Zhou, A.-H. Yuan, Y.-Z. Li, A series of novel cyano-bridged 4f–3d assemblies with achiral helical chains: syntheses, structures and magnetic properties, *Eur. J. Inorg. Chem.* (in press), <http://dx.doi.org/10.1002/ejic.201200354>.
- [10] S.-Y. Qian, H. Zhou, A.-H. Yuan, Y. Song, Syntheses, structures, and magnetic properties of five novel octacyanometalate-based lanthanide complexes with helical chains, *Cryst. Growth Des.* 11 (2011) 5676–5681.
- [11] L.D.C. Bok, J.G. Leipoldt, S.S. Basson, The preparation of Cs₃Mo(CN)₈·2H₂O and Cs₃W(CN)₈·2H₂O, *Z. Anorg. Allg. Chem.* 415 (1975) 81–83.
- [12] Crystal data for compounds **1** and **2**: C₃₆H₄₉MoN₁₅O₇Sm for compound **1**, *M_r* = 1050.19, monoclinic, space group *P*2₁/*c*, *a* = 11.3322(11), *b* = 21.212(2), *c* = 19.680(2) Å, *V* = 4587.6(8) Å³, *Z* = 4, *D_c* = 1.521 g cm⁻³, *R₁* (*wR₂*) = 0.0346 (0.0754) and *S* = 1.111 for 8588 reflections with *I* > 2σ(*I*). C₃₆H₄₉WN₁₅O₇Sm for compound **2**, *M_r* = 1138.10, monoclinic, space group *P*2₁/*c*, *a* = 11.3117(11), *b* = 21.186(2), *c* = 19.7165(19) Å, *V* = 4580.7(8) Å³, *Z* = 4, *D_c* = 1.650 g cm⁻³, *R₁* (*wR₂*) = 0.0338 (0.0753) and *S* = 1.190 for 9288 reflections with *I* > 2σ(*I*). Crystal structure measurements for compounds **1** and **2** were performed on a Bruker Smart Apex II CCD diffractometer using graphite-monochromatized Mo K_α radiation (λ = 0.71073 Å). Lorentz polarization and absorption corrections were applied. The structure was solved by direct methods and refined with the full-matrix least-squares technique using the *SHELXS-97* and *SHELXL-97* programs.
- [13] A.-H. Yuan, S.-Y. Qian, W.-Y. Liu, H. Zhou, Y. Song, Two octacyanometalate-based Ni(II)W(V) bimetallic assemblies with metamagnetism, *Dalton Trans.* 40 (2011) 5302–5306.
- [14] J. Wang, Y.-L. Xu, H.-B. Zhou, H.-S. Wang, X.-J. Song, Y. Song, X.-Z. You, Octacyanotungstate(V)-based square W₂M₂ (M = Co, Mn) complexes: synthesis, structure and magnetic properties, *Dalton Trans.* 39 (2010) 3489–3494.
- [15] H. Zhou, A.-H. Yuan, S.-Y. Qian, Y. Song, G.-W. Diao, Efficient synthetic strategy to construct three-dimensional 4f–5d networks using neutral two-dimensional layers as building blocks, *Inorg. Chem.* 49 (2010) 5971–5976.
- [16] R.L. Carlin, *Magnetochemistry*, Springer, Berlin, 1997.
- [17] S. Tanase, M. Evangelisti, L.J. de Jongh, Short-range correlations in d–f cyanido-bridged assemblies with XY and XY-Heisenberg anisotropy, *Dalton Trans.* 40 (2011) 8407–8413.
- [18] S.-L. Ma, S. Ren, Y. Ma, D.-Z. Liao, Sheet-like of Mo^V-Sm^{III} assembly containing [Mo^V(CN)₈]³⁻ and Sm³⁺ ions as building blocks, *J. Chem. Sci.* 121 (2009) 421–427.
- [19] P. Przychodzeń, R. Pełka, K. Lewiński, J. Supel, M. Rams, K. Tomala, B. Sieklucka, Tuning of magnetic properties of polynuclear lanthanide(III)-octacyanotungstate(V) systems: determination of ligand-field parameters and exchange interaction, *Inorg. Chem.* 46 (2007) 8924–8938.
- [20] P. Przychodzeń, K. Lewiński, R. Pełka, M. Bałanda, K. Tomala, B. Sieklucka, [Ln(terpy)]³⁺ (Ln = Sm, Gd) entity forms isolated magnetic chains with [W(CN)₈]³⁻, *Dalton Trans.* (2006) 625–628.
- [21] Y.-Z. Zhang, G.-P. Duan, O. Sato, S. Gao, Structures and magnetism of cyano-bridged grid-like two-dimensional 4f–3d arrays, *J. Mater. Chem.* 16 (2006) 2625–2634.
- [22] M. Estrader, J. Ribas, V. Tangoulis, X. Solans, M. Font-Bardía, M. Maestro, C. Diaz, Synthesis, crystal structure, and magnetic studies of one-dimensional cyano-bridged Ln³⁺-Cr³⁺ complexes with bpy as a blocking ligand, *Inorg. Chem.* 45 (2006) 8239–8250.
- [23] T. Hozumi, S. Ohkoshi, Y. Arimoto, H. Seino, Y. Mizobe, K. Hashimoto, Cooling-rate dependent ferromagnetism in a two-dimensional cyano-bridged Sm(III)-W(V) complex, *J. Phys. Chem. B* 107 (2003) 11571–11574.
- [24] H.-Z. Kou, S. Gao, X.-L. Jin, Synthesis, crystal structure, and magnetic properties of two cyano-bridged bimetallic 4f–3d arrays with one-dimensional chain and two-dimensional brick wall molecular structures, *Inorg. Chem.* 40 (2001) 6295–6300.
- [25] O. Kahn, *Molecular Magnetism*, VCH Publishers Inc., New York, 1993.