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Communication

Cyanide-Bridged One-Dimensional Ferromagnetic Ru^{III}Mn^{III} Coordination Polymer Exhibiting a Field-Induced Magnetic Phase Transition

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A cyanide-linked Ru^{III}(4d)−Mn^{III}(3d) bimetallic chain complex (**1**) was prepared by the self-assembly of a ruthenium(III) bicyanide and a Mn^{III} Schiff base. Ferromagnetic couplings between the magnetic centers are present within a chain, while antiferromagnetic interactions between chains (T_N = 2.5 K) transmit. Complex **1** also shows a field-induced magnetic phase transition.

The discovery of single-molecule magnets (SMMs) and single-chain magnets (SCMs) has fueled the quest for building up low-dimensional anisotropic magnetic systems.[1] One of the commonly attempted strategies is to employ molecular precursors that comprise blocking ligands and more than two bridging groups for incoming paramagnetic metal ions. Because cyanide can serve as a very efficient mediator of magnetic exchange, $[M(A)(CN)_p]^{n-}$ (M = paramagnetic metal ions, A = capping ligands, p = 1−6) units have become more popular for this purpose.[1b,2−4] Most related works have been concentrated on 3d−3d bimetallic assemblies utilizing 3d metal-based precursors with Fe^{III} (S_{Fe} = $^1/_2$) and Cr^{III} (S_{Cr} = $^3/_2$).[1b,2,3] In contrast, a limited number of 4d- or 5d-based cyanometalate precursors were successfully designed and applied to construct low-dimensional magnetic complexes exhibiting SMM, SCM, spin-canting, or metamagnetic characters.[4]

Recently, *trans*-ruthenium(III) bicyanides with spin-paired electron configuration t_{2g}^5 and thus spin S_{Ru} = $^1/_2$, which can be stabilized in coordination spheres encompassed by one salen [=*N,N*′-ethylenebis(salicylideneiminato) dianion] or two acac (=acetylacetonate) ligands, have attracted gradual attention and vindicated their performance as promising building blocks. For instance, these 4d moieties have produced 4d−3d families with discrete molecules, 1D, 2D, and 3D networks, as well as a 4d−4f series with 2D structures.[5,6] In view of the anticipated intriguing properties of low-dimensional anisotropic systems, such 1D coordination polymers are highly sought, and in this vein, we attempted to combine the *trans*-ruthenium(III)(salen) bicyanide and well-known anisotropic Mn^{III} centers coordinated by tetradentate Schiff bases.[7]

We report the synthesis, structure, and magnetic properties of a 1D chain [Ru(salen)(CN)$_2$][Mn(L)] (**1**) [L = *N,N*′-(1-methylethylene)bis(2-hydroxynaphthalene-1-carbaldehydene-iminate) dianion]. This complex marks a unique 1D Ru^{III}Mn^{III}

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(1) (a) Gatteschi, S.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268. (b) Lescouëzec, R.; Toma, L. M.; Vaissermann, J.; Verdaguer, M.; Delgado, F. S.; Ruiz-Pérez, C.; Lloret, F.; Julve, M. *Coord. Chem. Rev.* **2005**, *249*, 2691. (c) Coulon, C.; Miyasaka, H.; Clérac, R. *Struct. Bonding (Berlin)* **2006**, *122*, 163.

(2) (a) Li, D.; Parkin, S.; Wang, G.; Yee, G. T.; Clérac, R.; Wernsdorfer, W.; Holmes, S. M. *J. Am. Chem. Soc.* **2006**, *128*, 4214. (b) Yang, J. Y.; Shores, M. P.; Sokol, J. J.; Long, J. R. *Inorg. Chem.* **2003**, *42*, 1403. (c) Wang, S.; Zuo, J.-L.; Gao, S.; Song, Y.; Zhuo, H.-C.; Zhang, Y.-Z.; You, X.-Z. *J. Am. Chem. Soc.* **2004**, *126*, 8900. (d) Lescouëzec, R.; Vaissermann, J.; Toma, M.; Carrasco, R.; Lloret, F.; Julve, M. *Inorg. Chem.* **2004**, *43*, 2234. (e) Ni, Z.-H.; Kou, H.-Z.; Zhang, L.-F.; Ni, W.-W.; Jiang, Y.-B.; Cui, A.-L.; Ribas, J.; Sato, O. *Inorg. Chem.* **2005**, *44*, 9631. (f) Kim, J. I.; Yoo, H. S.; Koh, E. K.; Kim, H. C.; Hong, C. S. *Inorg. Chem.* **2007**, *46*, 8481. (g) Kim, J. I.; Yoo, H. S.; Koh, E. K.; Hong, C. S. *Inorg. Chem.* **2007**, *46*, 10461.

(3) (a) Zhang, Y.-Z.; Gao, S.; Wang, Z.-M.; Su, G.; Sun, H.-L.; Pan, F. *Inorg. Chem.* **2005**, *44*, 4534. (b) Pan, F.; Wang, Z.-M.; Gao, S. *Inorg. Chem.* **2007**, *46*, 10221. (c) Toma, L.; Lescouëzec, R.; Vaissermann, J.; Delgado, F. S.; Ruiz-Pérez, C.; Carrasco, R.; Cano, J.; Lloret, F.; Julve, M. *Chem.−Eur. J.* **2004**, *10*, 6130.

(4) (a) Shores, M. P.; Sokol, J. J.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 2279. (b) Schelter, E. J.; Prosvirin, A. V.; Dunbar, K. R. *J. Am. Chem. Soc.* **2004**, *126*, 15004. (c) Yoon, J. H.; Kim, H. C.; Hong, C. S. *Inorg. Chem.* **2005**, *44*, 7714. (d) Yoon, J. H.; Lim, J. H.; Kim, H. C.; Hong, C. S. *Inorg. Chem.* **2006**, *45*, 9613. (e) Yoon, J. H.; Lim, J. H.; Choi, S. W.; Kim, H. C.; Hong, C. S. *Inorg. Chem.* **2007**, *46*, 1529. (f) Choi, S. W.; Kwak, H. Y.; Yoon, J. H.; Kim, H. C.; Koh, E. K.; Hong, C. S. *Inorg. Chem.* **2008**, *47*, 10214.

(5) (a) Yeung, W.-F.; Man, W.-L.; Wong, W.-T.; Lau, T.-C.; Gao, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3031. (b) Yeung, W.-F.; Lau, P.-H.; Lau, T.-C.; Wei, H.-Y.; Sun, H.-L.; Gao, S.; Chen, Z.-D.; Wong, W.-T. *Inorg. Chem.* **2005**, *44*, 6579. (c) Toma, L. M.; Toma, L. D.; Delgado, F. S.; Ruiz-Pérez, C.; Sletten, J.; Cano, J.; Clemente-Juan, J. M.; Lloret, F.; Julve, M. *Coord. Chem. Rev.* **2006**, *250*, 2176. (d) Duimstra, J. A.; Stern, C. L.; Meade, T. J. *Polyhedron* **2006**, *25*, 2705.

(6) Yeung, W.-F.; Lau, T.-C.; Wang, X.-Y.; Gao, S.; Szeto, L.; Wong, W.-T. *Inorg. Chem.* **2006**, *45*, 6756.

(7) (a) Lecren, L.; Wernsdorfer, W.; Li, Y.-G.; Vindigni, A.; Miyasaka, H.; Clérac, R. *J. Am. Chem. Soc.* **2007**, *129*, 5045. (b) Mei, Y.; Zhao, F.; Zhang, W.; Pan, F.; Wang, Z.-M.; Gao, S. *Chem.−Eur. J.* **2007**, *13*, 2937.
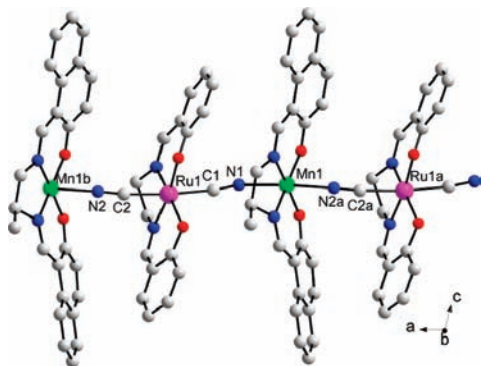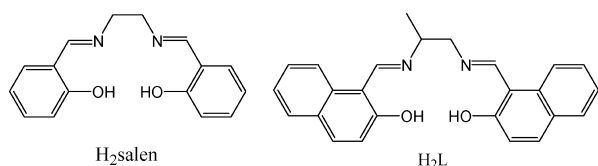
Figure 1. Molecular view of **1** with a selected atom-labeling scheme. Symmetry transformations used to generate equivalent atoms: $a = -1 + x, y, z$ and $b = 1 + x, y, z$.
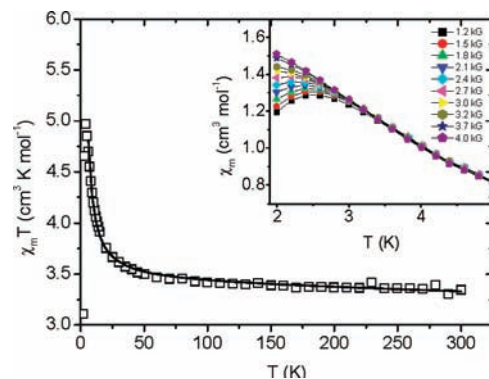

Figure 2. Temperature dependence of the $\chi_m T$ product for **1**. The solid line in the main panel shows the best fit to the magnetic model. The inset represents $\chi_m(T)$ curves in the low-temperature range and at indicated magnetic fields.

bimetallic material formed by the Mn^{III} Schiff base, displaying a field-induced magnetic phase transition.

H$_2$salen

H$_2$L

A stoichiometric reaction of [Ru(salen)(CN)$_2$]$^-$ with the manganese Schiff base produced red crystals of **1**.[8,9] The neutral linear 1D chain is formed by assembly of the [Ru(salen)(CN)$_2$]$^-$ anion and the [Mn(L)]$^+$ cation in which the CN groups act as bridges to two neighboring Mn^{III} centers in a trans mode (Figure 1).[10] The Ru^{III} center can be described as a distorted octahedral geometry consisting of two N atoms from CN ligands and two N and two O atoms from salen. The average Ru−N(O) bond length relevant with salen corresponds to 2.01(1) Å, whereas the mean Ru−C distance is somewhat longer, 2.06(1) Å. This trend agrees well with other Ru^{III}−M^{II} (M = Mn, Co, Ni) bimetallic complexes.[5] The Ru−C−N(cyanide) angles are virtually linear, 170.6(8)° for Ru1−C1−N1 and 169.9(9)° for Ru1−C2−N2. The central Mn^{III} ion adopts a tetragonally elongated octahedral environment as judged by the equatorial N$_2$O$_2$ plane constructed from L with a short average Mn−N(O) distance of 1.93(5) Å and the axial N atoms with significantly long distances [Mn1−N1 = 2.292(8) and Mn1−N2a = 2.307(8) Å; $a = -1 + x, y, z$]. This metrical disparity is definitely related to a high-spin octahedral Mn^{III} center, which originates from the Jahn−Teller distortion. The Mn−N−C(cyanide) angles, which are often magnetically important parameters along with the Mn−N(cyanide) length,

are alike, 144.3(8)° for Mn1−N1−C1 and 143.1(8)° for Mn1b−N2−C2 ($b = 1 + x, y, z$). It is noted that the angles are more acute than those of the Ru^{III}−M^{II} complexes in which the angles are larger than 164°.[5] The intrachain Ru−Mn separations are 5.197(2) Å for Ru1−Mn1 and 5.169(2) Å for Ru1−Mn1b, and the torsion angles of Ru−C≡N−Mn are 58.6(8)° for Ru1−C1−N1−Mn1 and 33.6(8)° for Ru1−C2−N2−Mn1b.

The crystal packing features 1D chains running along the a axis (Figures 1 and S1 in the Supporting Information). Two adjacent chains are correlated with extensive π−π stacking forces between naphthalene rings. The centroid distance is 3.619 Å and the interchain metal−metal distance is 10.823 Å through the noncovalent contacts. The shortest interchain metal−metal distance among other neighboring chains is 7.317 Å for Mn−Mn. Thus, the overall extended structure can be viewed as supramolecular 1D chains entangled with π−π stacks.

The magnetic susceptibility data for **1** were collected at 1 kG in the 2−300 K range, as plotted in Figure 2. The $\chi_m T$ value at 300 K is 3.35 cm^3 K mol^{-1}, which is close to the theoretical value (3.375 cm^3 K mol^{-1}) calculated from noncoupled Ru^{III} ($S_{Ru} = 1/2$) and Mn^{III} ($S_{Mn} = 2$) spins assuming $g = 2$. Lowering the temperature causes $\chi_m T$ to increase slowly until 30 K and abruptly reach a maximum of 4.97 cm^3 K mol^{-1} at 4 K. Below the peak temperature, $\chi_m T$ undergoes a sharp drop down to 3.11 cm^3 K mol^{-1} at 2 K. The continuous rise in $\chi_m T$ at temperatures higher than 4 K clearly indicates the operation of intrachain ferromagnetic couplings between Ru^{III} and Mn^{III} communicated by cyanide bridges. The downturn of $\chi_m T$ below 4 K pertains to zero-field splitting and/or interchain antiferromagnetic interactions. The magnetic data at $T > 10$ K were analyzed using the Curie−Weiss law [$\chi_m = C/(T - \theta)$], affording $C = 3.33$ cm^3 K mol^{-1} and $\theta = 2.5$ K. As a consequence, ferromagnetic interactions among paramagnetic centers are confirmed in this chain complex.

To examine the exchange coupling parameter between Ru^{III} and Mn^{III} spins, we used an analytical expression derived by Drillon et al. for the case of an alternating quantum-classical spin chain ($H = -J\sum_i S_i \cdot S_{i+1}$).[11] Because

(8) Leung, W.-H.; Che, C.-M. *Inorg. Chem.* **1989**, *28*, 4619.
(9) Preparation: Solid Na[Ru(salen)(CN)$_2$]$_8$ (0.1 mmol) was added to [Mn(L)(H$_2$O)]Cl (0.1 mmol) in a mixed solvent (MeOH:MeCN:DMF: H$_2$O = 10:5:2:1). After 1 min of stirring, the resulting red solution was filtered and then left undisturbed. The slow evaporation of the filtrate gave red crystals of **1** after several days. Yield: 81%. To grow single crystals suitable for X-ray, the proper solvent ratio was of utmost importance. Anal. Calcd for **1**·2.5H$_2$O: C, 57.4; H, 4.37; N, 9.34. Found: C, 57.1; H, 3.95; N, 9.79. IR cyanide stretching (cm^{-1}): 2131vw, 2095m.
(10) Crystal data for **1**: M = 855.77, triclinic, space group P$\bar{1}$, $a = 10.3451(13)$ Å, $b = 11.8813(15)$ Å, $c = 15.996(19)$ Å, $\alpha = 105.739(5)°$, $\beta = 105.119(4)°$, $\gamma = 90.070(4)°$, $V = 1776.3(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.598$ g cm^{-3}, $\mu = 0.836$ mm^{-1}, $T = 130$ K, R1 = 0.0839, wR2 = 0.1289 [$I > 2\sigma(I)$].
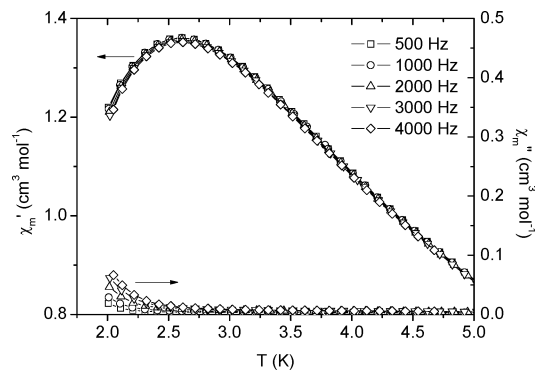(11) Drillon, M.; Coronado, E.; Beltran, D.; Georges, R. *Chem. Phys.* **1983**, *79*, 449.

Figure 3. Plots of χ_m' and χ_m'' vs T for **1** at zero dc field, an ac field of 5 G, and several indicated oscillating frequencies.

Figure 4. Field dependences of the magnetizations for **1** at 2, 3, and 4 K.

the low-spin Ru^{III} ion in the octahedral ligand field possesses not only spin but also unquenched orbital angular momentum as well, this isotropic model would provide approximate magnetic parameters. A best fit to the data in the temperature range of 6–300 K resulted in roughly estimated values of g_{Ru} = 2.14, g_{Mn} = 1.99, and J = 1.34 cm^{-1}.[12] The positive J value is indicative of the presence of ferromagnetic interactions between the spin centers via the CN linkage. As far as orbital models for magnetic interaction are concerned, the total magnetic coupling constant (J) is the summation of antiferromagnetic (J_{AF}) and ferromagnetic (J_F) terms. When the $d\pi$ orbitals on Ru^{III} and Mn^{III} are overlapped, antiferromagnetic interactions (J_{AF}) will emerge. In contrast, the Ru $d\pi$ orbitals and Mn d_{z^2} orbital are orthogonal because of π/σ-type symmetry, which is expected to provide ferromagnetic routes (J_F). The orbital overlaps (J_{AF}) would be substantially reduced as inferred from the relatively long Mn–N(cyanide) length and the bent Mn–N–C(cyanide) angles largely deviated from 180°.[13] This structural situation will render the ferromagnetic term (J_F) to overwhelm the antiferromagnetic contribution (J_{AF}), finally facilitating such ferromagnetic coupling in **1**.

The alternating current (ac) susceptibility data (Figure 3) demonstrate that frequency-independent maxima in χ_m' are evident at T_N = 2.5 K, accompanied by no peaks in χ_m'' at the same temperature, designating the occurrence of a long-range antiferromagnetic order.[14] This trait emanates from antiferromagnetic interactions among 1D chains. The low-temperature χ_m' and χ_m'' signals are slightly frequency-dependent, which is a signature of a glassy magnetized state probably reminiscent of SCM-like behavior or spin canting. Because the aniferromagnetic order arising from the inter-chain antiferromagnetic interactions is present in **1**, spin canting, which is in conjunction with single-ion anisotropy of Ru^{III} and Mn^{III}, may be more feasible. The similar characteristics were also observed in antiferromagnetic
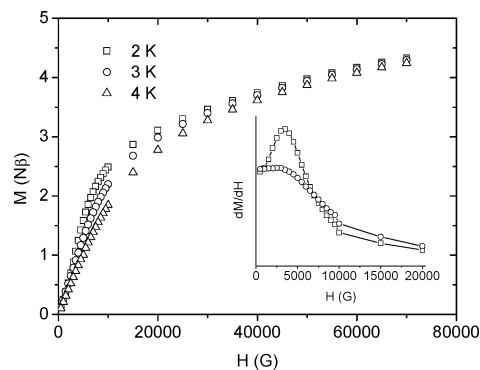
complexes with single-ion anisotropy and/or antisymmetric exchange.[15]

The field-dependent magnetizations were measured at 2, 3, and 4 K in the 0–7 T scope (Figure 4). The magnetization value at 2 K and 7 T amounts to 4.33 Nβ, which is slightly lower than the ferromagnetic result (5 Nβ) calculated from $M_S = g(S_{Ru} + S_{Mn})$ with g = 2. This difference is concerned with the magnetic anisotropy of **1**. A field-induced spin-flop or metamagnetic transition occurs at H_c = 3.5 kG as determined by the dM/dH curve in the inset of Figure 4. This phenomenon was frequently revealed in antiferromagnets including magnetic anisotropy.[2g,4c,16] To further inspect the magnetic behavior, we recorded $\chi_m(T)$ data at several fields as plotted in the inset of Figure 2. The peaks at 2.5 K obviously exist at lower magnetic fields, and above H_c, the peaks are completely suppressed, reflecting the onset of the magnetic phase transition upon rising field.

In summary, we have prepared and characterized the first Ru^{III}–Mn^{III} bimetallic chain by self-assembly of $[Ru(salen)(CN)_2]^-$ and the magnetic anisotropic Mn Schiff base. The intrachain ferromagnetic couplings between Ru^{III} and Mn^{III} are established through the CN ligands, whereas the interchain antiferromagnetic interactions subsist, leading to an antiferromagnet with T_N = 2.5 K. Notably, a field-induced magnetic phase transition is observed as well in **1**.

Supporting Information Available: X-ray crystallographic file in CIF format and additional structural and magnetic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Mn^{III} was assumed to act as a classical spin carrier with S_{Mn} = 2, leading to an effective alternating chain with S_{Mn} = 2 and S_{Ru} = $^1/_2$. The magnetic model may be roughly applied to the system with the quantum spin S_{Ru}= $^1/_2$.

(13) Miyasaka, H.; Saitoh, A.; Abe, S. *Coord. Chem. Rev.* **2007**, *251*, 2622.

(14) (a) Zeng, M.-H.; Zhang, W.-X.; Sun, X.-Z.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3079. (b) Rabu, P.; Rueff, J. M.; Huang, Z. L.; Angelov, S.; Souletie, J.; Drillon, M. *Polyhedron* **2001**, *20*, 1677.

(15) (a) Lu, Y.-B.; Wang, M.-S.; Zhou, W.-W.; Xu, G.; Guo, G.-C.; Huang, J.-S. *Inorg. Chem.* **2008**, *47*, 8935. (b) Palii, A. V.; Reu, O. S.; Ostrovsky, S. M.; Klokishner, S. I.; Tsukerblat, B. S.; Sun, Z.-M.; Mao, J.-G.; Prosvirin, A. V.; Zhao, H.-H.; Dunbar, K. R. *J. Am. Chem. Soc.* **2008**, *130*, 14729. (c) Ko, H. H.; Lim, J. H.; Kim, H. C.; Hong, C. S. *Inorg. Chem.* **2006**, *45*, 8847.

(16) (a) Manson, J. L.; Huang, Q.-z.; Lynn, J. W.; Koo, H.-J.; Whangbo, M.-H.; Bateman, R.; Otsuka, T.; Wada, N.; Argyriou, D. N.; Miller, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 162. (b) Li, W.; Ju, Z.-F.; Yao, Q.-X.; Zhang, J. *CrystEngComm* **2008**, *10*, 1325. (c) Li, W.; Jia, H.-P.; Ju, Z.-F.; Zhang, J. *Dalton Trans.* **2008**, 5350.