

Scientific paper

# Two Binuclear Cyanide-bridged Cr(III)-Mn(III) Complexes Based-on [Cr(2,2'-bipy)(CN)<sub>4</sub>]<sup>-</sup> Building Block: Synthesis, Crystal Structures and Magnetic Properties

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## Abstract

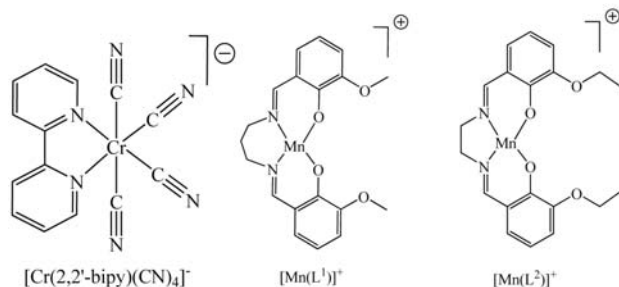
Tetracyanide building block [Cr(2,2'-bipy)(CN)<sub>4</sub>]<sup>-</sup> and two bicompartimental Schiff-base based manganese(III) compounds have been employed to assemble cyanide-bridged heterometallic complexes, resulting in two cyanide-bridged Cr<sup>III</sup>-Mn<sup>III</sup> complexes: [Mn(L<sup>1</sup>)(H<sub>2</sub>O)][Cr(2,2'-bipy)(CN)<sub>4</sub>] · CH<sub>3</sub>OH · 2.5H<sub>2</sub>O (**1**) and [Mn(L<sup>2</sup>)(H<sub>2</sub>O)][Cr(2,2'-bipy)(CN)<sub>4</sub>] · CH<sub>3</sub>OH · 3H<sub>2</sub>O (**2**) (L<sup>1</sup> ≡ *N,N'*-(1,3-propylene)-bis(3-methoxysalicylideneimine), L<sup>2</sup> ≡ *N,N'*-ethylenebis(3-ethoxysalicylideneimine)). Single-crystal X-ray diffraction analysis shows their similar cyanide-bridged binuclear structures, in which the cyanide precursor acts as monodentate ligand connecting the manganese(III) ion. The binuclear complexes are self-complementary through coordinated aqua ligand and the free O<sub>4</sub> compartment from the neighboring complex, giving H-bond linking dimer structure. Investigations on magnetic properties reveal the antiferromagnetic coupling between the cyanide-bridged Cr(III) and Mn(III) ions. By using a Fortran program through numerical matrix diagonalization techniques, a best-fit to the magnetic susceptibilities of these two complexes leads to the magnetic coupling constants  $J \equiv -5.95 \text{ cm}^{-1}$ ,  $j \equiv -0.61 \text{ cm}^{-1}$  (**1**) and  $J \equiv -4.15 \text{ cm}^{-1}$ ,  $j \equiv -0.57 \text{ cm}^{-1}$  (**2**), respectively.

**Keywords:** Cyanide-bridged, heterometallic complex, crystal structure, magnetic property.

## 1. Introduction

During the past several decades, there has been great interest in cyanide-bridged bimetallic assemblies.<sup>1–6</sup> The main interest in such compounds arises from their magnetic properties, since the short cyanide bridge mediates efficiently the magnetic interactions (either ferro- or antiferromagnetic) between the metal centers. Furthermore, based-on the symmetry of the magnetic orbitals from the magnetic point of view, it is possible to predict the nature of the magnetic exchange between the cyanide-bridged paramagnetic metal ions by using simple orbital models. Therefore, up to now, a large amount of cyanide-bridged magnetic complexes with divers structures from 0D cluster to 3D network and interesting magnetic properties, such as highest  $T_C$  molecule-based materials, molecule-based photomagnets, spin crossover materials, single-molecule magnets (SMMs), and single-chain magnets (SCMs),<sup>7–23</sup> have been successfully synthesized, structurally characterized and magnetically investigated.

The current main synthetic route for cyanide-bridged system is to decrease the number of cyanide ligands of the hexa- or octacyanometalate [M(CN)<sub>6/8</sub>]<sup>n-</sup> precursor by blocking some of its coordination sites with chelating ligands. This strategy provides better control of the dimensionality of the final outcome when carefully selecting the building blocks of both the negative charged [M(L)(CN)<sub>x</sub>]<sup>n-</sup> and the positive charged [M'(L')<sub>y</sub>]<sup>m+</sup>. Considering that it is an effective mean to increase the strength of the magnetic exchange coupling comparable to the low spin Fe(III) ion, several chromium-containing cyanide building blocks have been designed and used to assemble cyanide-bridged magnetic complexes.<sup>24–29</sup> Here, we investigated the reactions of K[Cr(2,2'-bipy)(CN)<sub>4</sub>] with two bicompartimental Schiff-base manganese(III) compounds (Scheme 1), which have been proved as good candidates for assembling heterobimetallic cyanide-bridged system with interesting magnetic properties.<sup>30–31</sup> Synthesis, crystal structures and magnetic properties of



Scheme 1. The starting reactants used for the synthesis of **1** and **2**.

two new binuclear cyanide-bridged Cr(III)-Mn(III) complexes,  $[\text{Mn}(\text{L}^1)(\text{H}_2\text{O})][\text{Cr}((2,2'\text{-bipy})(\text{CN})_4)] \cdot \text{CH}_3\text{OH} \cdot 2.5\text{H}_2\text{O}$  (**1**) and  $[\text{Mn}(\text{L}^2)(\text{H}_2\text{O})][\text{Cr}((2,2'\text{-bipy})(\text{CN})_4)] \cdot \text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$  (**2**), which can be further dimerized by intermolecular hydrogen bond interactions, will be described in this paper.

## 2. Experimental Section

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El. The infrared spectroscopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer in the 4000–400  $\text{cm}^{-1}$  region. Variable-temperature magnetic susceptibility and field dependence magnetization measurements were performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

**General procedures and materials.** All the reactions were carried out under an air atmosphere and all chemicals and solvents used were reagent grade without further purification.  $\text{K}[\text{Cr}((2,2'\text{-bipy})(\text{CN})_4)]$  was synthesized as described in literature,<sup>24</sup> and the  $[\text{Mn}(\text{L}^1/\text{L}^2)(\text{H}_2\text{O})_2]\text{ClO}_4$  were available from the previous work.<sup>32</sup>

**Preparation of Complexes 1 and 2.** These two target complexes were prepared using the similar procedure. To a solution of  $[\text{Mn}(\text{L}^1/\text{L}^2)(\text{H}_2\text{O})_2]\text{ClO}_4$  (57.4 mg/58.8 mg, 0.10 mmol) in methanol (10 mL),  $\text{K}[\text{Cr}((2,2'\text{-bipy})(\text{CN})_4)]$  (39.5 mg, 0.10 mmol) dissolved in methanol/water (1:4, v:v) (10 mL) was carefully added. The resulting mixture was filtered at once and the filtrate was kept undisturbed at room temperature. After one week, brown-black block crystals were collected by filtration.

**Complex 1:** Yield: 42.5 mg, 53%. Anal. Calcd. for  $\text{C}_{34}\text{H}_{39}\text{CrMnN}_8\text{O}_{8.5}$ : C, 50.88; H, 4.90; N, 13.96. Found: C, 51.04; H, 4.01; N, 13.79. Main IR bands ( $\text{cm}^{-1}$ ): 3400 (s), 2160, 2125 (s,  $\nu_{\text{C}\equiv\text{N}}$ ), 1620–1640 (vs,  $\nu_{\text{C}\equiv\text{N}}$ ), 1495 (m), 1355 (m), 1100 (m), 1000(s).

**Complex 2:** Yield: 38.8 mg, 47%. Anal. Calcd. for  $\text{C}_{35}\text{H}_{42}\text{CrMnN}_8\text{O}_9$ : C, 50.91; H, 5.12; N, 13.57. Found: C, 51.18; H, 4.31; N, 13.49. 3400 (s), 2162, 2126 (s,  $\nu_{\text{C}\equiv\text{N}}$ ), 1620–1640 (vs,  $\nu_{\text{C}\equiv\text{N}}$ ), 1500 (m), 1355 (m), 1095 (m), 1000(s).

### X-ray data collection and structure refinement.

Single crystals of both complexes with suitable dimensions for X-ray diffraction analysis were mounted on the glass rod and the crystal data were collected on a Bruker SMART CCD diffractometer with a Mo- $K_{\alpha}$  sealed tube ( $\lambda \equiv 0.71073 \text{ \AA}$ ) at 293 K, using a scan mode. The structures were solved by direct method and refined using Fourier difference techniques with the SHELXTL-97 program package. The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced as fixed contributors. All the nonhydrogen atoms except the disordered ones were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients  $U(\text{H}) \equiv 1.2U(\text{C})$  or  $1.5U(\text{C})$  and their coordinates were allowed to ride on their respective carbons using SHELXL97 except some of the H atoms of the solvent molecules. Those H atoms were refined isotropically with fixed  $U$  values and the DFIX command was used to rationalize the bond parameter. CCDC 1024295 and 1024296 for these two complexes contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via . Details of the crystal parameters, data collection, and refinement are summarized in Table 1.

Table 1. Crystallographic data for complexes **1** and **2**.

	<b>1</b>	<b>2</b>
Formula	$\text{C}_{34}\text{H}_{39}\text{CrMnN}_8\text{O}_{8.5}$	$\text{C}_{35}\text{H}_{42}\text{CrMnN}_8\text{O}_9$
$F_w$	802.67	825.71
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
$a/\text{\AA}$	22.3274(18)	15.216(10)
$b/\text{\AA}$	14.7217(12)	15.491(10)
$c/\text{\AA}$	23.2155(18)	17.603(14)
$\alpha/\text{deg}$	90	90
$\beta/\text{deg}$	98.2820(10)	93.895(11)
$\gamma/\text{deg}$	90	90
$V/\text{\AA}^3$	7551.3(10)	4140(5)
$Z$	8	4
$F(000)$	3328	1716
$\theta/\text{deg}$	1.66 to 25.00	1.71 to 25.00
$GOF$	1.095	1.009
$R_1[I > 2\sigma(I)]$	0.0534	0.0826
$wR_2$ (all data)	0.1679	0.2438

## 3. Results and Discussion

### 3. 1. Synthesis and General Characterization.

In our recent works,<sup>30–31</sup> the Mn(III) compounds containing the bicompartimental Schiff-base ligands,  $\text{H}_2$ -3-MeO-salen and  $\text{H}_2$ -3-EtO-salen (salen  $\equiv N,N$ -ethylene-bis(salicylideneimine)) have been successfully employed to assembly cyanide-bridged heterometallic complexes

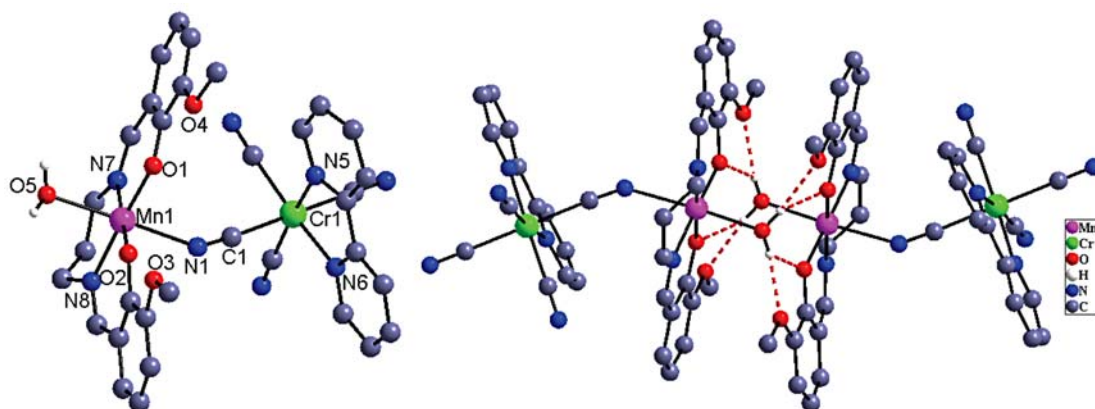
with interesting magnetic properties by using polycyano-metalates as building blocks. Furthermore, the obtained results indicated that the length of the substitute group on the Schiff-base have obvious influence on the structure of the cyanide-bridged complexes. With these in mind, we further investigated the reactions of the bicompartimental Schiff-base manganese compounds  $[\text{Mn}(\text{L}^1/\text{L}^2)(\text{H}_2\text{O})_2]\text{ClO}_4$  with tetracyanide-containing building block  $\text{K}[\text{Cr}((2,2'\text{-bipy})(\text{CN})_4)]$ , and obtained two binuclear heterobimetallic cyanide-bridged Cr(III)-Mn(III) complexes. In the IR spectra of complexes **1** and **2**, two sharp peaks with similar intensity due to the cyanide-stretching vibration were observed at about 2120 and 2150  $\text{cm}^{-1}$ , respectively, indicating the presence of bridging and nonbridging cyanide ligands in these complexes.

### 3. 2. Crystal Structures of Complexes 1 and 2.

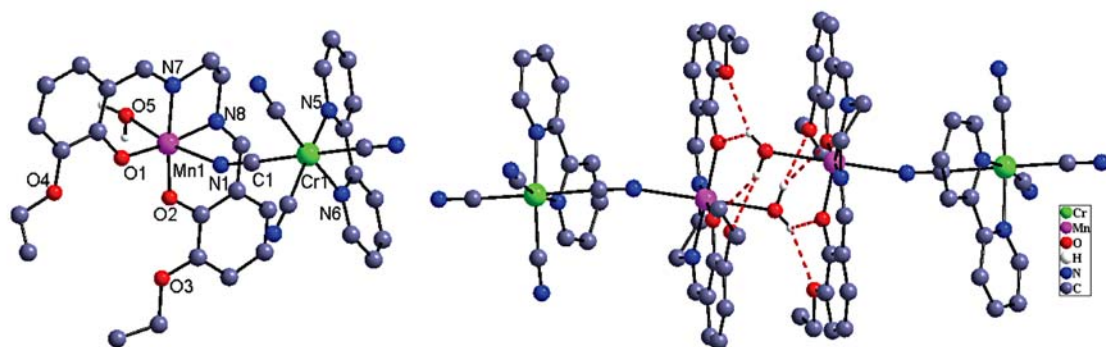
Some important structural parameters for complexes **1** and **2** are collected in Table 2. Their neutral binuclear structures, the dimers constructed by intermolecular hydrogen bond interactions and the cell packing diagram for complex **1** are shown in Figures 1–3, respectively.

As can be found, the structures of complexes **1** and **2** belong to cyanide-bridged bimetallic binuclear type. In each of these two complexes, Cr(III) and Mn(III) ion are linked through an axial cyanide group of the  $[\text{Cr}(2,2'\text{-bipy})(\text{CN})_4]^-$  moiety acting as a monodentate ligand. The Cr(III) ion is hexacoordinated, forming a slightly distorted octahedron surrounded by two N atoms of the chelating 2,2'-bipy ligand and four cyanide-C atoms, what can be proven by the bond parameters around the Cr(III) atom. The  $\text{Cr}-\text{C}_{\text{cyanide}}-\text{N}_{\text{cyanide}}$  bond angle is very similar in both complexes **1** and **2** with the value close to  $180^\circ$ , indicating that these three atoms are in a good linear conformation.

The coordination sphere of the Mn ion in both complexes can also be described as a distorted octahedral, in which four equatorial positions are occupied by two N atoms and two O atoms from the Schiff-base ligand, and the axial positions are occupied by N atoms of the bridging cyanide group and O atom of the coordinated water molecule. As shown in Table 2, distances between the Mn atom and the N, O atoms of the Schiff-base ligand (1.871–2.032 Å) are obviously shorter than the  $\text{Mn}-\text{N}_{\text{cyanide}}$  and  $\text{Mn}-\text{O}_{\text{water}}$  bond lengths (2.195(3)–2.312(7) Å), which



**Figure 1.** The neutral binuclear structure (left) and the dimer constructed by intermolecular hydrogen bond interactions (right) for complex **1**. Solvent molecules and the hydrogen atoms not involved in hydrogen-bonding have been omitted for clarity.



**Figure 2.** The neutral binuclear structure (left) and the dimer constructed by intermolecular hydrogen bond interactions (right) for complex **2**. Solvent molecules and the hydrogen atoms not involved in hydrogen-bonding have been omitted for clarity.

gives further information about the axial elongation of the Mn(III) surrounding, typically accounting for the well known Jahn-Teller effect. For the C≡N–Mn angle in these two complexes, there exists slightly conspicuous difference with the values of 145.4(4) and 157.7(7)°, respectively, indicative that these three atoms substantially deviate from a linear configuration. These bond parameters are basically consistent with those found in the reported complexes based on the same cyanide precursor and similar Schiff-base manganese compounds.<sup>28,29</sup> As shown in Figures 1 and 2, the binuclear complexes are self-complementary through coordinated aqua ligand from one complex and the free O<sub>4</sub> compartment from the neighboring complex, giving a hydrogen bond linking dimer structure, which is similar to that for the reported cyanide-bridged binuclear complex.<sup>29</sup> Furthermore, the abundant intermolecular hydrogen-bond interaction of

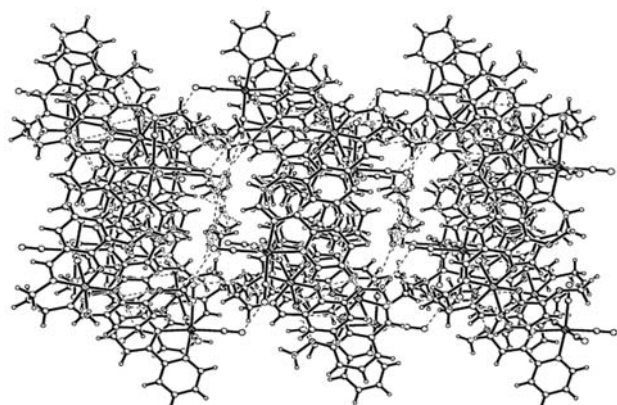


Figure 3. The cell packing diagram along *b* for complex **1**.

Table 2. Selected bond lengths (Å) and angles (°) for complexes **1** and **2**.

	<b>1</b>	<b>2</b>
Mn1–N1	2.283(4)	2.312(7)
Mn1–N7	2.032(3)	1.987(8)
Mn3–N8	2.021(3)	1.984(6)
Mn1–O1	1.891(2)	1.871(5)
Mn1–O2	1.886(2)	1.879(6)
Mn1–O5	2.195(3)	2.268(5)
Cr1–C1	2.071(5)	2.105(9)
Cr 1–C2	2.066(5)	2.046(9)
Cr 1–C3	2.040(5)	2.042(10)
Cr 1–C4	2.053(5)	2.062(10)
Cr 1–N5	2.076(3)	2.075(7)
Cr 1–N6	2.074(3)	2.072(7)
C1–N1–Mn1	145.4(4)	157.7(7)
O5–Mn1–N1	171.16(11)	169.7(2)
N1–C1–Cr 1	175.7(4)	177.0(8)
N2–C2–Cr 1	177.9(6)	174.1(9)
N3–C3–Cr 1	177.6(5)	175.0(9)
N4–C4–Cr 1	175.8(4)	177.0(10)

O–H···O can be found, which in turn results in 2D supramolecular network structure. The intramolecular cyanide-bridged Cr<sup>III</sup>–Mn<sup>III</sup> and the intermolecular Mn–Mn separation between the dimer are 5.226, 4.899 and 5.435, 4.880 Å in complexes **1** and **2**, respectively, while the shortest intermolecular metal-metal distance is markedly longer than the above separation with the value of about 7.594 and 9.132 Å.

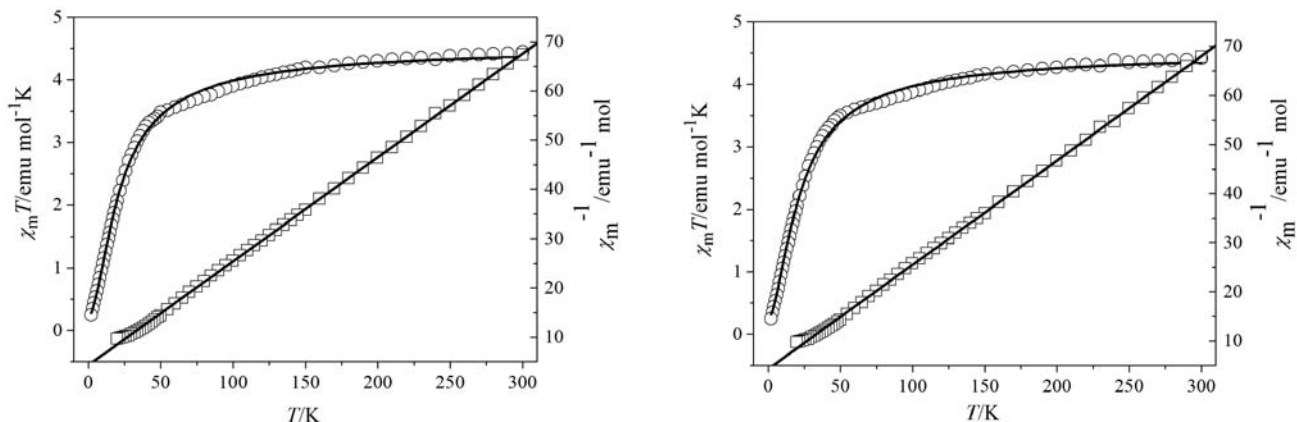
### 3. 3. Magnetic Properties of Complexes **1** and **2**.

The temperature dependences of magnetic susceptibilities measured in the temperature range of 2–300 K in the applied field of 2000 Oe for complexes **1** and **2** are given in Figure 4. The room temperature  $\chi_m T$  values of these two complexes are 4.42 and 4.45 emu K mol<sup>-1</sup>, respectively, which are slightly lower than the spin only value of 4.875 emu K mol<sup>-1</sup> for uncoupled Mn(III) ( $S \equiv 5/2$ ) and Cr(III) ( $S \equiv 3/2$ ) based on  $g \equiv 2.00$ . With the temperature decreasing, the  $\chi_m T$  value decreases gradually and attains the value of about 3.5 emu K mol<sup>-1</sup> for these two complexes at about 50 K, then decreases sharply to the lowest value about 0.25 emu K mol<sup>-1</sup> at 2 K. The magnetic susceptibilities for these two complexes conform Curie-Weiss law in the range of 20–300 K and give the negative Weiss constant  $\theta \equiv -20.43$  K and Curie constant  $C \equiv 4.70$  emu K mol<sup>-1</sup> for **1** and  $\theta \equiv -20.58$  K and  $C \equiv 4.74$  emu K mol<sup>-1</sup> for **2**, respectively. The negative Weiss constant as well as the change tendency of the  $\chi_m T$ - $T$  give information that there exist overall antiferromagnetic interactions between the Cr(III) and Mn(III) ions bridged by cyanide group in the two complexes.

According to the crystal structures of these two complexes, two main exchange pathways are responsible for their cryomagnetic behaviour: the intramolecular interaction mediated by the cyanido bridge, and the interaction at the supramolecular level, mediated by the hydrogen bonds linking the two manganese Schiff-base units. To evaluate the strength of intra-/inter-dimer magnetic coupling ( $J$  and  $j$ ) and zfs parameter ( $D$ ) of Mn(III) ion, the following spin Hamiltonian has been used to analyze the magnetic data of complexes **1** and **2**.<sup>29,34</sup>

$$\hat{H} \equiv -2JS_{Cr}S_{Mn} - 2jS_{Mn}S_{Mn'} + D_{Mn}(\hat{S}_z^2 - S_{Mn}(S_{Mn} + 1/3)) + g\beta H\hat{S}$$

The magnetic data for these two compounds have been simulated through numerical matrix diagonalization techniques, using a Fortran program.<sup>33</sup> The best-fit parameters obtained are  $J \equiv -5.95$  cm<sup>-1</sup>,  $j \equiv -0.61$  cm<sup>-1</sup>,  $g \equiv 2.01$ ,  $D_{Mn} \equiv -3.1$  cm<sup>-1</sup>,  $R \equiv 2.54 \times 10^{-5}$  for complex **1** ( $R$  is the agreement factor defined as  $\sum(\chi_{\text{obsd}}T - \chi_{\text{cald}}T)^2 / \sum(\chi_{\text{obsd}}T)^2$ ) and  $J \equiv -4.15$  cm<sup>-1</sup>,  $j \equiv -0.57$  cm<sup>-1</sup>,  $g \equiv$



**Figure 4.** Temperature dependences of  $\chi_m T$ - $T$  (the solid line represents the best fit based on the parameters discussed in the text) for complex **1** (left) and **2** (right). Inset: Temperature dependences  $\chi_m^{-1}$ - $T$  (the solid line was calculated from the Curie-Weiss law).

2.00,  $D_{Mn} \equiv -3.3 \text{ cm}^{-1}$ ,  $R \equiv 3.19 \times 10^{-5}$  for complex **2**, respectively. These results are comparable to those found in other cyanide-bridged Cr(III)-Mn(III) complexes.<sup>29</sup> Also, as has been proved by Gao's group,<sup>28</sup> the dependence of the exchange constant ( $J$ , in  $\text{cm}^{-1}$ ) on  $\theta$  (in degrees for Mn-C≡N angle) in the cyanide-bridged Cr(III)-Mn(III) system follows a linear relationship  $J \equiv -33 + 0.18\theta$ . According to this relationship, the expected values of  $J$  for our two complexes would be  $-6.85$  and  $-4.62 \text{ cm}^{-1}$ , respectively, which are also comparable to our fitting results obtained above.

## 4. Conclusion

In summary, two new cyanide-bridged Cr(III)-Mn(III) complexes structurally characterized as heterobimetallic binuclear type have been synthesized with tetracyanide-containing precursor  $\text{K}[\text{Cr}(2,2'\text{-bipy})(\text{CN})_4]$  as building block and two bicompartimental Schiff-base manganese(III) compounds as assemble segments. Investigations on their magnetic properties reveal an overall antiferromagnetic interaction between the cyanide-bridged Cr-Mn metal centers. The results further confirm the facts that this type of cyanidometallate precursors are suitable building blocks to prepare cyanide-bridged magnetic complexes with diverse structure types and there is always antiferromagnetic coupling between the cyanide-bridged Cr(III) ion and Mn(III) ion.

## 5. Acknowledgement

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## Povzetek

Spojini  $[\text{Mn}(\text{L}^1)(\text{H}_2\text{O})][\text{Cr}(\text{2,2}'\text{-bipy})(\text{CN})_4] \cdot \text{CH}_3\text{OH} \cdot 2.5\text{H}_2\text{O}$  (**1**) in  $[\text{Mn}(\text{L}^2)(\text{H}_2\text{O})][\text{Cr}(\text{2,2}'\text{-bipy})(\text{CN})_4] \cdot \text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$  (**2**) ( $\text{L}^1 \equiv N,N'$ -(1,3-propilen)-bis(3-metoksisalicilideniminat),  $\text{L}^2 \equiv N,N'$ -etilen-bis(3-etoksisalicilideniminat)), kjer sta različna kovinska centra povezana z mostovnim cianido ligandom, sta bili pripravljene iz tetracianido strukturnega elementa  $[\text{Cr}(\text{2,2}'\text{-bipy})(\text{CN})_4]^-$  in dveh manganovih(III) koordinacijskih spojin z dvopredelno Schiffovo bazo. Rentgenska monokristalna analiza je razkrila nastanek podobnih dvojedrnih struktur s cianidnim mostovnim ligandom, pri katerih je cianidni prekurzor kot enovezni ligand koordiniran na manganov(III) ion. Pri obeh kristalnih strukturah dvojedrna zvrst tvori dimer povezan preko koordinirane vode in prostega O4 predela sosednje molekule. Preiskava magnetnih lastnosti pokaže antiferomagnetno sklopitev med Cr(III) in Mn(III) ionoma povezanima s cianidnim ligandom. Z uporabo programa Fortran preko diagonalizacijskih metod z numeričnimi maticami vodi najboljše ujemanje pri magnetni susceptibilnosti teh dveh spojin k magnetni sklopitveni konstanti  $J \equiv -5.95 \text{ cm}^{-1}$ ,  $j \equiv -0.61 \text{ cm}^{-1}$  (**1**) oziroma  $J \equiv -4.15 \text{ cm}^{-1}$ ,  $j \equiv -0.57 \text{ cm}^{-1}$  (**2**).