Polynuclear and one-dimensional cyanide-bridged heterobimetallic complexes: synthesis, crystal structures and magnetic properties

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Abstract. Three new heterobimetallic cyanide-bridged complexes, $\{[\text{Ni}(\text{L}^1)]\text{Ag}(\text{CN})_2\}[\text{Ag}(\text{CN})_2] \cdot 2\text{H}_2\text{O}$ (**2**), $\{[\text{Mn}(\text{L}^2)]\text{Ag}(\text{CN})_2\} \cdot 1.5\text{H}_2\text{O}$ (**3**) and $\{[\text{Mn}(\text{L}^3)(\text{H}_2\text{O})]_2[\text{Ag}(\text{CN})_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ (**4**) ($\text{L}^1 = 2,7,12$ -trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene; $\text{L}^2 = \text{N,N}'$ -1,3-propylene-bis(5-chlorosalicylideneimine); $\text{L}^3 = \text{N,N}'$ -1,2-propylene-bis(5-bromosalicylideneimine)), have been assembled using for the first time a new polyaza macrocycle nickel(II) compound $[\text{Ni}(\text{L}^1)](\text{ClO}_4)_2$ (**1**), or Schiff-base manganese(III) compounds and $\text{K}[\text{Ag}(\text{CN})_2]$. Single crystal X-ray diffraction analysis reveals that complexes **2** and **3** can be characterized as one-dimensional cationic and neutral single chain structure, respectively. Complex **3** forms a three-dimensional network *via* weak inter-chain $\text{Ag} \dots \text{Ag}$ interactions. Complex **4** belongs to a cyanide-bridged bimetallic sandwich-like cationic trinuclear structure containing Mn_2Ag core with free ClO_4^- as a counter anion, indicating that the Schiff-base ligand has an obvious influence on the structure of the cyanide-bridged complexes formed. Investigation of the magnetic susceptibilities of the cyanide-bridged Ag-Ni(II)/Mn(III) complexes showed the weak anti-ferromagnetic interaction between neighboring paramagnetic Ni(II) or Mn(III) ions bridged by the long NC-Ag-CN unit. From the best-fit of the magnetic susceptibility data of complexes **2** and **4** the magnetic coupling constant was determined to be $J = -0.51$ and -0.78 cm^{-1} , respectively.

Keywords. Cyanide-bridged complex; heterobimetallic complex; crystal structure; magnetic property.

1. Introduction

In the recent past decades, many effective strategies have been developed to rationally assemble metal complexes with diversified topological structures and interesting properties with the ultimate goal of obtaining molecular materials with new structures, properties and functions. Due to the significant role of the cyanide group as a remarkable linker in tuning the magnetic coupling between the paramagnetic centers and excellent stabilizing ability on a variety of transition metal centers with or without the peripheral ligands, the cyanide-bridged magnetic complexes have been widely studied in the field of molecular magnetism.^{1–6} Usually the rational design of cyanide-bridged magnetic systems is achieved following the practical method of assembling appropriate

cyanide precursors exhibiting targeted chemical and physical properties (local anisotropy, spin state, etc.) and various paramagnetic metal ions with or without the ancillary organic ligands, which have resulted in many cyanide-bridged complexes with diverse structures and interesting magnetic properties.^{7–27}

The peripheral ligands attached to the paramagnetic counterpart assembled segment have an obvious influence on the structure of the resulting complexes. Therefore, for the purpose of tuning the structure of the cyanide-bridged complexes, many mono- or multi-dentate organic ligands with different structures and steric effects have been used to block the paramagnetic metal ions. Among which, we are interested in *quasi*-planar macrocyclic and Schiff-base ligands. The polyaza semi-rigid macrocyclic ligands obtained by condensation of 2,6-diacetylpyridine and polyamine have proven to be good ancillary ligands to assemble

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cyanide-bridged complexes. Some Ni(II), Mn(II) or Fe(II) complexes with different structures and interesting magnetic properties based on the above polyaza macrocyclic ligand have been reported.^{28–33} On the other hand, due to their facile preparation, and more importantly due to the large spin state ($S = 2$) as well as the usual negative magnetic anisotropy of the central Mn(III) ion, which can sometime result in interesting magnetic phenomena, the Schiff-base manganese(III) compounds based on quasi-planar tetradentate N_2O_2 or N_2O_4 Salen-type ligands (Salen = N,N-bis(salicylidene)ethane-1,2-diamine) have drawn much interest for constructing molecular magnets.^{4–6}

$[Ag(CN)_2]^-$ with two cyanide groups in a *trans* position can be used to assemble 1D to 3D coordination polymers based on the coordination bond and Ag...Ag interactions. Several silver polymer examples with diverse structures and interesting optical properties have been reported.^{34–36} In this paper, we report the investigation of the reactions of *trans*-dicyanometallate $K[Ag(CN)_2]$ with a new macrocyclic nickel compound $[Ni(L^1)](ClO_4)_2$ (**1**), whose structure has also been crystallographically characterized, or Schiff-base manganese(III) compounds, resulting in three cyanide-bridged bimetallic complexes with different structure types formulated as $\{[Ni(L^1)][Ag(CN)_2][Ag(CN)_2] \cdot 2H_2O$ (**2**), ($L^1 = 2,7,12$ -trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene), $\{[Mn(L^2)][Ag(CN)_2]\} \cdot 1.5H_2O$ (**3**) and $\{[Mn(L^3)(H_2O)]_2[Ag(CN)_2]ClO_4 \cdot 2H_2O$ (**4**) ($L^2 = N,N'$ -1,3-propylene-bis(5-chlorosalicylideneimine); $L^3 = N,N'$ -1,2-propylene-bis(5-bromosalicylideneimine)). The synthesis, crystal structures and magnetic properties for the above mentioned four complexes are presented here. The results provide some meaningful information for the designed synthesis of low-dimensional cyanide-bridged bimetallic complexes with the macrocyclic nickel or manganese Schiff-base compound as assembled segments.

2. Experimental

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El. The infrared spectra on KBr pellets were performed on a Magna-IR 750 spectrophotometer in the 4000–400 cm^{-1} region. Variable temperature magnetic susceptibility and field dependent 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).

2.1 General Procedures and Materials

All the chemicals and solvents used were reagent grade and used without further purification. All the reactions were carried out in air atmosphere. $[NiL^1](ClO_4)_2$ was prepared according to the reported method for its analogue with slight modification.³⁷ The two Schiff-base manganese compounds were synthesized by the method described in the literature.³⁸

Caution! KCN is hypertoxic and hazardous. Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled in small quantities with care.

2.2 The synthesis of compound 1

To an ethanol solution (60 mL) of 2,6-Diacetylpyridine (3.26 g, 0.02 mol) was added Nickel(II) perchlate hexahydrate (7.3 g, 0.02 mol). The mixture solution was heated to about 65 °C and 2.9 g 0.02 mol) of 3,3'-diamino-(N-methyl) dipropylamine was added, and the solution was refluxed for about 6 h, after which the solution was condensed on a rotary evaporator to reduce the volume of the solution to about 15 mL. After filtering the remaining solution to remove the tiny insoluble materials, excess of ether was added to precipitate the target compound. The product was collected by filtration, washed with ether and dried in air. Yield: about 65%. Anal. Calcd. for $C_{16}H_{24}Cl_2N_4NiO_8$: C, 36.26; H, 4.57; N, 10.57%. Found: C, 36.21; H, 4.51; N, 10.68%.

2.3 The synthesis of complex 2

To a solution of $[NiL^1](ClO_4)_2$ (52.9 mg, 0.10 mmol) in methanol (10 mL), $K[Ag(CN)_2]$ (19.9 mg, 0.20 mmol) dissolved in methanol/water (4:1, v:v) (10 mL) was carefully added. The resulting mixture was filtered at once and the filtrate was kept undisturbed at room temperature in the dark. After two weeks, dark-brown block crystals were collected by filtration with the yield of 42.0 mg, 63.6%. $\mu_{eff} = 2.83$ B.M. Anal. Calcd. For $C_{19}H_{26.5}Ag_2N_7NiO_2$: C, 34.61; H, 4.05; N, 14.87%. Found: C, 34.49; H, 3.85; N, 14.68%. Main IR bands (cm^{-1}): 2125, 2160 (s, $\nu_{C\equiv N}$), 1615, 1625 (vs, $\nu_{C=N}$).

2.4 The synthesis of complexes 3 and 4

A solution containing $K[Ag(CN)_2]$ (19.9 mg, 0.10 mmol) dissolved in 5 mL of distilled water was laid in the bottom of a tube, upon which a mixed solvent of water and acetonitrile and methanol with a ratio of 1:2:1 was carefully added. Then, $[Mn(L^2)(H_2O)_2]ClO_4$ (54 mg, 0.10 mmol) or $[Mn(L^3)(H_2O)_2]ClO_4$ (62.9 mg, 0.10 mmol) dissolved in a mixture (5 mL) of CH_3OH and CH_3CN was carefully added to the top of the mixed solvent layer. Single crystals suitable for X-ray diffraction were obtained from the solvent layer after one/two weeks, which were then collected by filtration and dried in air.

Complex 3: Yield 35.1 mg, 59.4%. $\mu_{eff} = 5.91$ B.M. Anal. Calcd. for $C_{19}H_{17}AgCl_2MnN_4O_{3.5}$: C, 38.61; H, 2.90; N,

Table 1. Crystallographic data for complexes **1–4**.

	1	2	3	4
Chemical Formula	C ₁₆ H ₂₄ Cl ₂ N ₄ NiO ₈	C ₁₉ H _{26.5} Ag ₂ N ₇ NiO ₂	C ₁₉ H ₁₇ Ag Cl ₂ MnN ₄ O _{3.5}	C ₃₆ H ₃₆ AgBr ₄ ClMn ₂ N ₆ O ₁₂
Fw	530.00	659.42	591.08	1317.55
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	Pna2(1)	Fdd2	C2/c	C2/c
<i>a</i> /Å	12.2052(8)	19.819(3)	17.371(6)	21.745(5)
<i>b</i> /Å	14.0267(9)	50.218(6)	12.723(4)	16.123(5)
<i>c</i> /Å	12.7334(9)	10.5278(13)	20.224(7)	15.260(4)
α /deg	90	90	90	90
β /deg	90	90	103.639(6)	113.580(7)
γ /deg	90	90	90	90
<i>V</i> /Å ³	2179.9(3)	10478(2)	4344(3)	4903(2)
<i>Z</i>	4	16	8	4
Completeness	99.9%	98.5%	99.0%	99.7%
<i>F</i> (000)	1096	5240	2344	2576
θ /deg	2.16 to 25.01	1.62 to 25.01	2.00 to 25.02	1.62 to 25.01
<i>GOF</i>	1.081	1.063	1.072	1.039
<i>R</i> ₁ [<i>I</i> > 2(<i>I</i>)]	0.0361	0.0878	0.0537	0.0698
<i>wR</i> ₂ (all data)	0.1003	0.2659	0.1617	0.2395

Scheme 1. The starting materials used to prepare the complexes **2–4**.

9.48%. Found: C, 38.71; H, 2.81; N, 9.36%. Main IR bands (cm^{−1}): 2125 (s, $\nu_{\text{C}\equiv\text{N}}$), 1620, 1625 (vs, $\nu_{\text{C}\equiv\text{N}}$).

Complex 4: Yield 40 mg, 60.7%. $\mu_{\text{eff}} = 5.91$ B.M. Anal. Calcd. For C₃₆H₃₆AgBr₄ClMn₂N₆O₁₂: C, 32.81; H, 2.75; N, 6.38%. Found: C, 32.70; H, 2.65; N, 6.29%. Main IR bands (cm^{−1}): 2122 (s, $\nu_{\text{C}\equiv\text{N}}$), 1622, 1627 (vs, $\nu_{\text{C}\equiv\text{N}}$), 1100 (s, $\nu_{\text{Cl-O}}$).

2.5 X-ray Data Collection and Structure Refinement

The crystal data were collected on an Oxford Diffraction Gemini E diffractometer with Mo *K*α radiation ($\lambda =$

0.71073 Å) at the room temperature. Final unit cell parameters were derived by global refinements of reflections obtained from integration of all the frame data. CrysAlisPro Agilent Technologies software was used to collect frames of data and for the determination of lattice constants. The structures were solved by the direct method (*SHELXS-97*) and refined by full-matrix least-squares (*SHELXL-97*) on *F*².³⁹ The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced as fixed contributors. All the non-hydrogen atoms, except the disordered ones, were refined with anisotropic displacement coefficients. For the disordered contents, the partially occupied atoms were refined isotropically. Hydrogen atoms were added geometrically and refined using a riding model, except some of the solvent H atoms.

For these H atoms, they were refined isotropically with fixed U values and the DFIX command was used to rationalize the bond parameter. The crystallographic data for complexes **1–4** are listed in Table 1. CCDC 1575943–1575946 for complexes **1–4** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and Discussion

3.1 Synthesis and general characterization

As shown in Scheme 1, similar to its analogue $[\text{NiL}]^{37}$ (ClO_4)₂ ($\text{L} = 2,12$ -trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene), which has been proved to be an excellent candidate to assemble cyanide-bridged magnetic complexes, the new macrocyclic nickel compound $[\text{NiL}^1](\text{ClO}_4)_2$ (**1**) contains 14-membered polyaza macrocycle which adopts a planar conformation. A tetragonal geometry on the central metal ion with different electronic configuration is imposed, leading to the stabilization of the six-coordinated species. Therefore, as expected, the reaction between the *trans*- $\text{K}[\text{Ag}(\text{CN})_2]$ and the newly synthesized nickel compound results in the one-dimensional infinite cyanide-bridged Ni-Ag complex. Considering that the *trans*- $[\text{Ag}(\text{CN})_2]^-$ is a good linear cyanide precursor and more in favor of forming 1D structure, we investigated the reactions of this building block with two Schiff-base manganese(III) compound, which has two replaceable *trans* positions, and obtained two cyanide-bridged Ag-Mn complexes with different structures, indicating that different Schiff-base ligands have obvious influence on the structure of the target complexes.

All the cyanide-bridged complexes have been characterized by IR spectroscopy. In the IR spectra of complex **2**, the two sharp peaks due to the cyanide-stretching vibration were observed in the range of 2120 and 2160 cm^{-1} , respectively, indicating the presence of bridging and non-bridging cyanide ligands in these complexes. For complexes **3** and **4**, the single peak at about 2125 cm^{-1} can be assigned to the bridging cyanide group. Observation of a strong broad peak centered at ca. 1100 cm^{-1} for complexes **1** and **4** suggests the presence of ClO_4^- anion.

3.2 Crystal Structure of Complexes 1–4

Some important structural parameters for complexes **1–4** are collected in Tables 2 and 3. The cationic mononuclear structure of complex **1** is shown in Figure 1. For complex **2**, asymmetric cationic binuclear unit

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

1		2	
Ni(1)–N(1)	1.814(4)	Ni(1)–N(1)	2.12(3)
Ni(1)–N(2)	1.922(3)	Ni(1)–N(2)	2.14(3)
Ni(1)–N(3)	1.923(3)	Ni(1)–N(4)	1.944(10)
Ni(1)–N(4)	1.945(4)	Ni(1)–N(5)	2.079(14)
Cl(1)–O(1)	1.392(5)	Ni(1)–N(6)	2.085(12)
Cl(1)–O(2)	1.344(5)	Ni(1)–N(7)	2.056(14)
Cl(1)–O(3)	1.373(6)		
Cl(1)–O(4)	1.330(5)	C(1)–N(1)–Ni(1)	168.1(2)

Table 3. Selected bond lengths (Å) and angles (°) for complexes **3** and **4**.

	3	4
Mn(1)–N(1)	2.242(6)	2.264(9)
Mn(1)–N(2)	2.260(6)	1.969(9)
Mn(1)–N(3)	2.026(5)	1.983(9)
Mn(1)–N(4)/O4	2.054(6)	2.317(7)
Mn(1)–O(1)	1.896(5)	1.861(7)
Mn(1)–O(2)	1.883(5)	1.889(7)
C(1)–N(1)–Mn(1)	168.0(6)	163.6(11)

Figure 1. The cationic mononuclear structure of the compound **1**. Displacement ellipsoids are drawn at 30% probability level. The ClO_4^- anions and all the H atoms have been omitted for clarity.

and the one-dimensional cationic single chain structure are shown in Figure 2. As can be found, the mononuclear $[\text{Ni}(\text{L}^1)]^{2+}$ cation contains the four-coordinated nickel ion, for which the four coordination positions are from

Figure 2. The asymmetric cationic unit and one-dimensional cationic infinite structure of complex 2. Displacement ellipsoids are drawn at the probability level of 30%. All the hydrogen atoms, the solvent molecules and the free $[\text{Ag}(\text{CN})_2]^-$ have been omitted for clarity.

Figure 3. The asymmetric unit and the neutral one-dimensional chain structure of complex 3. Displacement ellipsoids are drawn at the 30% probability level. All the H atoms and the solvent molecules have been omitted for clarity.

Figure 4. The two-dimensional double-layer supramolecular structure for complex **3** constructed by the weak Ag...Ag interactions. All the H atoms and the solvent molecules have been omitted for clarity.

the four N atoms of the macrocyclic ligand, thus forming a *quasi*-planar square geometry with unhindered axial sites.

X-ray diffraction reveals the one-dimensional cationic infinite structure of complex **2**, comprising of repeating $[-\text{NC-Ag-CN-Ni}(\text{L}^1)-]$ unit with the positive charge balanced by the disordered $[\text{Ag}(\text{CN})_2]^-$ anion. Each $[\text{Ag}(\text{CN})_2]^-$ unit, acting as a bidentate ligand through its two *trans* cyanide groups, connects the Ni(II) ions of two independent macrocyclic nickel units. The Ni ion is coordinated by four N atoms of the macrocyclic ligand located in the equatorial plane and two N atoms of the bridge cyanide groups in *trans* position. The Ni-N_{macrocyclic} bond lengths are 1.944(10), 2.079(14), 2.085(12) and 2.056(14) Å, which are basically consistent with the corresponding distances in the mononuclear compound **1** (Table 2) but slightly shorter than the Ni-N_{cyanide} bond lengths with the values 2.14(3) and 2.12(3) Å, indicating that the coordination sphere of the Ni atom is a slightly distorted octahedron. The Ni-N $\equiv$ C bond angle is a little bent from the linear conformation with the value of 168.1(2)°. The intramolecular Ni^{II}-Ni^{II} separation through bridging cyanide precursor is about 10.53 Å.

Some selected bond distances and bond angles for complexes **3** and **4** are collected in Table 3. The asymmetric unit, the neutral one-dimensional chain and the two-dimensional double-layer supramolecular structure for complex **3** are shown in Figures 3 and 4, respectively. For complex **4**, its cationic trinuclear structure and the cell packing diagram are depicted in Figure 5.

Complexes **3** and **4**, which contain eight and four independent units in the unit cell, crystallize in the same monoclinic cell setting C2/c space group but

Figure 5. The cationic trinuclear structure and the cell packing diagram along *b* axis for complex **4**. Displacement ellipsoids are drawn at 30% probability level. All the non-solvent H atoms except those of the water molecules have been omitted for clarity.

with different structural types. Complex **3** possesses a neutral infinite linear chain structure consisting of alternate Ag(I) and Mn(III) ions. In the chains, each *trans*- $[\text{Ag}(\text{CN})_2]^-$ connects two $[\text{Mn}(\text{L}^2)]^+$ with two *trans*-cyanide groups, and in turn, each *trans*- $[\text{Mn}(\text{L}^2)]^+$ unit links two *trans*- $[\text{Ag}(\text{CN})_2]^-$ building blocks, in which the $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Mn}(\text{L}^2)]^+$ groups are disposed parallel to each other. It should be noted that the 1D chain structure of the complex **3** can be further extended into the supramolecular 3D network with the help of weak Ag...Ag interactions between the different chains in vertical directions. Different from that of the complex **3**, the structure of the complex **4** belongs to cyanide-bridged cationic sandwich-like type containing trinuclear Mn_2Ag core, in which the cyanide precursor anion acting as bidentate ligand connects two Schiff-base manganese(III) units through its two *trans* cyanide groups, with positive charge balanced by the free ClO_4^- anion.

Figure 6. The $\chi_m T$ and χ_m^{-1} vs T curves for complex **2** (left) and complex **4** (right). The solid lines represent to the best fit curves.

The Mn(III) ion in the complexes **3** and **4** is six-coordinated, forming a slightly distorted octahedral coordination geometry, in which the four equatorial positions are occupied by N_2O_2 unit coming from the Schiff-base ligand, two axial ones coordinated by two N atoms of cyanide groups in complex **3**, and one cyanide N atom and one O atom of the coordinated water molecule in complex **4**. As shown in Table 3, the Mn–N_{cyanide} and Mn–O_{water} bond lengths with the values 2.242(6), 2.260(6), 2.264(9) and 2.317(7) Å, respectively, are obviously longer than the average Mn–N_{Schiff-base} and Mn–O_{Schiff-base} bond lengths within the range of 1.969(9)–2.054(6) and 1.861(7)–1.896(5) Å, which give rise to an elongated octahedral geometry around the Mn(III), with the Jahn-Teller axis lying along the z direction, i.e., the N_{cyanide}–Mn–N_{cyanide} axis. The Mn–N $\equiv$ C bond angles in these two complexes are 168.0(6) and 163.6(11)°, respectively, indicating that these three atoms deviate slightly from a linear configuration. The intramolecular distances between the two Mn(III) ion bridged by the long diamagnetic $[Ag(CN)_2]^-$ are 10.766 in **3** and 10.750 Å in **4**, respectively.

3.3 Magnetic properties of complexes 2–4

As described above, the $[Ni(L^1)]^{2+}$ is a planar diamagnetic compound, while the six-coordinated paramagnetic Ni(II) ions in the complex are bridged by the cyanide precursor. For complexes **3** and **4**, from the molecular magnetism of the view, both the complexes contain the diamagnetic cyanide building block-bridged Mn(III) ions. Therefore, investigation of the magnetic properties of the complexes, with complexes **2** and **4** as representatives, were carried out, and the temperature dependence of magnetic susceptibility for these

two complexes were measured in the range of 2–300 K under the external magnetic field of 2000 Oe. These are shown in Figure 6. The room temperature values of $\chi_m T$ are 0.95 and 2.96 emu K mol^{−1} for complexes **2** and **4**, respectively, slightly lower than the spin only value 1.0 and 3.0 emu K mol^{−1} for the isolated Ni(II) ($S = 1$) ion and the Mn(III) ($S = 2$) ion with $g = 2.0$. With the lowering of temperature, the $\chi_m T$ value remains almost constant until about 50 K, and then decreases rapidly to the lowest value of 0.615 and 1.614 emu K mol^{−1} at 2.0 K. The magnetic susceptibility obeys Curie-Weiss law in the range of 20–300 K, and affords negative Weiss constant $\theta = -2.91$ K and Curie constant $C = 1.16$ emu K mol^{−1} for complex **2**, and $\theta = -3.98$ K and Curie constant $C = 2.84$ emu K mol^{−1} for complex **4**. This primarily indicates that the antiferromagnetic coupling between the cyanide-bridged Ni(II) or Mn(III) ion in these two complexes.

The magnetic properties for complexes **2** and **4** have been simulated by using the dimeric model with the following Hamilton, in which the zero-split effect of the Mn(III) ion in complex **4** was considered due to its obviously elongated octahedral coordination sphere, typical of the Jahn-Teller effect.⁴⁰

$$H = -2JS_1S_2$$

$$H = -2JS_1S_2 + D_1[S_{1z}^2 - 1/3S_1(S_1 + 1)] \\ + D_2[S_{2z}^2 - 1/3S_2(S_2 + 1)]$$

The magnetic data between 2–300 K were fitted, resulting in the best fitting parameters which match the experimental data are $J = -0.51$ cm^{−1}, $g = 2.01$ and $J = -0.78$ cm^{−1}, $D = -1.91$ cm^{−1}, $g = 2.02$ for complexes **2** and **4**, respectively. The small J values can be attributed to the long distance between the paramagnetic metal ions separated by the long diamagnetic dicyanometallate.

4. Conclusions

In summary, with a new macrocyclic Nickel(II) compound, structurally confirmed for the first time, and two different Schiff-base Manganese(III) compounds as assembling segments and *trans*-dicyanometallate as a building block, three new heterobimetallic cyanide-bridged complexes have been synthesized and structurally characterized as one-dimensional polymer or cationic trinuclear entity. For the 1D cyanide-bridged Mn(III)-Ag(I) compound, the one-dimensional chain can be further extended into three-dimensional supramolecular structure depending on the weak Ag...Ag interactions between the adjacent chains in the vertical directions. Investigation of the magnetic properties of complexes **2-4** showed weak anti-ferromagnetic coupling between neighboring Ni(II) or Mn(III) ions.

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