Syntheses, Crystal Structures and Magnetic Properties of two Heterometallic Cyanide-Bridged $[M^{II}_2Mn^{II}_2]$ ($M = Fe$ and Os) Square Complexes

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Abstract: Two tetra-nuclear cyanide-bridged square complexes [*cis*-Fe(bpy)₂(CN)₂Mn(L)]₂-[PF₆]₄ (**1**) and [*cis*-Os(bpy)₂(CN)₂Mn(L)]₂[PF₆]₂[ClO₄]₂ (**2**) (bpy = 2, 2'-bipyridine, L = 1,6-diphenyl-2,5-bis(2-methylpyridyl)-2,5-diazahehexane) were synthesized and fully characterized. The tetranuclear [*cis*-M(bpy)₂(CN)₂Mn(L)]₂⁴⁺ (M = Fe (**1**), Os (**2**)) cation is composed of two [M(bpy)₂(CN)₂] and two [Mn(L)]²⁺ centers. Each M^{II} ion adopts a distorted [MN₄C₂] octahedral coordination, surrounding by four nitrogen atoms from two bpy ligands and two carbon atoms from the cyanide groups in a *cis* position. Each Mn²⁺ ion

also adopts a distorted [MnN₆] octahedral coordination, occupied by four nitrogen atoms from **L** and two nitrogen atoms from the cyanide groups in a *cis* position. The magnetic susceptibilities measurements indicate **1** is weak ferromagnetic, and **2** is weak antiferromagnetic.

Key words: Cyanide-Bridged, Tetra-nuclear Square, Magnetic Properties, Heterometallic

1. Introduction

Recently, considerable attention has been focused on the design and preparation of polynuclear metal complexes with predictable and controllable topology by self-assembling methods.[1-3] The topological control is indeed of outstanding interest when preparing molecular materials because their physical properties strongly depend on their architectures, especially when dealing with magnetic properties. As one of the most important magnetic systems, cyanide-bridged complexes have received much attention.[4-11] The cyanide-bridged complexes are attractive not only because the cyanide group can efficiently propagate magnetic and electronic interactions between metallic fragments, but also because their molecular topological structures and magnetic coupling between neighboring metal ions through the cyanide bridge can be controlled and predicted. In the past two decades, a number of cyanide-bridged molecule-based magnetic materials including high T_c [12-14], single-molecule magnets (SMMs)[15-18], single-chain magnets (SCMs)[19-23], spin crossover (SCO)[24-27], and photomagnetic materials[28-31] have been synthesized and investigated. The cyanide-bridged complexes with various structures have been structurally and magnetically characterized on the rational selection of paramagnetic centers and coordinated ligands. However, much effort in this field has been devoted to the study of the cyanide-bridged

compounds in which the paramagnetic metal ions are directly bridged by the CN^- ions, and the magnetic investigation of those paramagnetic metal ions separated by diamagnetic cyanidometal bridge has been paid much less attention. To date, only a few such examples have been reported.[32-40]

Recently, our group has been interested in the investigation of polynuclear compounds with a bridging diamagnetic cyanidometal ligand.[41-47] In this paper, we report the syntheses, crystal structures, electronic absorption spectroscopy and magnetic properties of two tetra-nuclear cyanide-bridged square complexes $[\text{cis-Fe}(\text{bpy})_2(\text{CN})_2\text{Mn}(\text{L})]_2[\text{PF}_6]_4$ (**1**), $[\text{cis-Os}(\text{bpy})_2(\text{CN})_2\text{Mn}(\text{L})]_2\text{PF}_6]_2[\text{ClO}_4]_2$ (**2**).

2. Experimental Section

2.1 Physical measurements

Elemental analyses (C, H, N) were carried out on a Vario MICRO elemental analyzer. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using KBr pellets. UV-vis spectrum was measured on a Perkin-Elmer Lambda 900 UV-vis-NIR spectrophotometer. Direct current magnetic susceptibilities and field dependences of the magnetization were carried out using a Quantum Design Magnetic Property Measurement System (MPMS) SQUID-XL. Alternating current (AC) magnetic susceptibilities were conducted on a Physical Property Measurement System (PPMS) PPMS-9T. Diamagnetic corrections for complexes **1** and **2** were made using Pascal's constants.

2.2 Materials and syntheses

All manipulations were performed under argon atmosphere with the use of standard Schlenk techniques unless otherwise depicted. Methanol was dried by distillation over magnesium. Diethyl ether was dried by distillation over sodium wire under an argon atmosphere. DMF was dried by distillation over MgSO_4 . 1,6-diphenyl-2,5-bis(2-methylpyridyl)-2,5-diazaheptane (**L**)[48], *cis*- $\text{Fe}(\text{bpy})_2(\text{CN})_2 \cdot 3\text{H}_2\text{O}$ [49, 50] and *cis*- $\text{Os}(\text{bpy})_2(\text{CN})_2 \cdot 7\text{H}_2\text{O}$ [51, 52] were prepared according to the literature procedures. All other reagents were available commercially and used without further purification.

2.3 Synthesis of [*cis*- $\text{Fe}(\text{bpy})_2(\text{CN})_2\text{Mn}(\text{L})$] $_2[\text{PF}_6]_4$ (**1**)

To a 25 ml methanol solution of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (61.2mg, 0.250mmol), 1.1 equiv of **L** (116.1mg, 0.275mmol) was added at room temperature and stirred for 0.5 h. Then *cis*- $\text{Fe}(\text{bpy})_2(\text{CN})_2 \cdot 3\text{H}_2\text{O}$ (100 mg, 0.211 mmol) was added to the mixture. The reaction mixture was heated to 60 °C and stirred for 6 h, resulting in a purple solution. NH_4PF_6 (37.8 mg, 0.232 mmol) was then added to the above reaction solution. A red precipitate appeared immediately and was collected. Deep red crystals (130 mg, 52%) of **1** suitable for X-ray diffraction were obtained by slowly diffusing diethyl-ether into the DMF solution of the red precipitate at room temperature. Anal. Calc. for $\text{C}_{100}\text{H}_{92}\text{F}_{24}\text{Fe}_2\text{Mn}_2\text{N}_{20}\text{P}_4$: C, 50.56; H, 3.90; N, 11.79%. Found: C, 50.37; H, 3.41; N, 11.77%. IR (KBr pellet, cm^{-1}): 2091 (CN). UV-vis (CH_3CN), λ_{max} , nm (ϵ , $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 359 (15240), 524 (14731).

2.4 Synthesis of [*cis*- $\text{Os}(\text{bpy})_2(\text{CN})_2\text{Mn}(\text{L})$] $_2[\text{PF}_6]_2[\text{ClO}_4]_2$ (**2**)

Compound **2** was prepared using the same procedure as for compound **1**, except for the addition of *cis*- $\text{Os}(\text{bpy})_2(\text{CN})_2 \cdot 7\text{H}_2\text{O}$ (144 mg, 0.211 mmol) and $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (76.4mg, 0.211mmol) instead of *cis*- $\text{Fe}(\text{bpy})_2(\text{CN})_2 \cdot 3\text{H}_2\text{O}$ and $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$. Yield brown black crystals (105 mg,

39%). Anal. Calc. for $C_{100}H_{92}Cl_2F_{12}Mn_2N_{20}O_8Os_2P_2$: C, 47.05; H, 3.63; N, 10.97%. Found: C, 46.94; H, 3.79; N, 10.93%. IR (KBr pellet, cm^{-1}): 2070 (CN), 2053(CN). UV-vis (CH_3CN), λ_{max} , nm (ϵ , $dm^3 mol^{-1} cm^{-1}$): 346(17176), 416(17477), 450(19525), 579(5002).

2.5 Crystallographic Data and structure determination

The single crystal data of complexes **1** and **2** were collected on Saturn724+ CCD diffractometers equipped with graphite-monochromatic Mo K_{α} ($\lambda = 0.71073 \text{ \AA}$) radiation using an ω scan mode at 123 K. The structures were solved by direct methods and refined using the *SHELXL-97* program suite[53, 54]. Hydrogen atoms were calculated geometrically and refined using a riding model. Anisotropic thermal parameters were used for the non-hydrogen atoms, and isotropic parameters were used for the hydrogen atoms. All non-hydrogen atoms were refined by full-matrix least-squares on F^2 . The R values are defined as $\omega R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $\omega R_2 = [\Sigma[\omega(F_o^2 - F_c^2)^2]/\Sigma[\omega(F_o^2)^2]]^{1/2}$. The detailed crystal data for complexes **1** and **2** were summarized in Table 1, and selected bond lengths and angles for complexes **1** and **2** were presented in Table 2.

Table 1 Detail of the Crystallographic Data Collection, Structural Determination and Refinementfor Complexes **1** and **2**.

	1	2
Chemical formula	C ₁₀₀ H ₉₂ F ₂₄ Fe ₂ Mn ₂ ON ₂₀ P ₄	C ₁₀₀ H ₉₂ Cl ₂ F ₁₂ Mn ₂ N ₂₀ O ₈ Os ₂ P ₂
Formula weight	2391.40	2553.06
Colour and Habit	Red Prism	Brown Prism
Crystal Size / mm	0.52×0.36×0.10	0.37×0.29×0.19
<i>T</i> / K	123	123
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / Å	16.247(6)	16.361(6)
<i>b</i> / Å	21.438(7)	21.952(7)
<i>c</i> / Å	16.361(6)	16.577(6)
<i>α</i> / deg	90	90
<i>β</i> / deg	114.787(6)	117.242(5)
<i>γ</i> / deg	90	90
<i>V</i> / Å ³	5174(3)	5294(3)
<i>Z</i>	2	2
<i>D</i> _{calc} / g cm ⁻³	1.535	1.602
<i>μ</i> / mm ⁻¹	0.678	2.792
Completeness	97.9%	99.6%
<i>F</i> (000)	2436	2540
<i>h</i> , <i>k</i> , <i>l</i> , range	-20≤ <i>h</i> ≤21, -27≤ <i>k</i> ≤27, -21≤ <i>l</i> ≤15	-21≤ <i>h</i> ≤20, -28≤ <i>k</i> ≤28, -21≤ <i>l</i> ≤21
<i>θ</i> range (deg)	2.35-27.47	2.32-27.48
Reflections measured	11595	12100
Independent reflections	10407	10165
Params/Restraints/ Data(obs.)	748/90/11595	667/186/12100
<i>R</i> _{int}	0.0668	0.0470
GOF	1.060	1.032
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> >2σ(<i>I</i>)]	0.0776, 0.2077	0.0644, 0.1707
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0834, 0.2161	0.0759, 0.1820

Table 2. Selected Bond Length (Å) and Bond Angle (°) for Complexes **1** and **2**

	1	2
M1-C1	1.890(3)	1.977(7)
M1-C2	1.895(3)	1.980(6)
M1-N3	1.991(3)	2.127(6)
M1-N4	1.943(3)	2.055(8)
M1-N5	1.984(3)	2.084(8)
M1-N6	2.007(3)	2.137(8)
Mn1-N1	2.141(3)	2.123(6)
Mn1-N2	2.133(3)	2.135(6)
Mn1-N7	2.290(3)	2.276(5)
Mn1-N8	2.353(3)	2.366(5)
Mn1-N9	2.346(3)	2.368(5)
Mn1-N10	2.272(3)	2.288(6)
C1≡N1	1.157(4)	1.164(9)
C2≡N2	1.161(5)	1.138(8)
C1-M1-C2	93.12(13)	93.6(3)
N2-Mn1-N1	96.39(11)	98.9(2)
N1≡C1-M1	175.8(3)	175.9(6)
N2≡C2-M1	171.2(3)	173.3(6)
C1≡N1-Mn1	152.1(3)	143.3(6)
C2≡N2-Mn1	148.1(3)	149.1(6)

3. Results and Discussion

3.1 Synthesis and Characterization

Tetra-nuclear cyanide-bridged square complexes $[cis\text{-Fe}(\text{bpy})_2(\text{CN})_2\text{Mn}(\text{L})_2][\text{PF}_6]_4$ (**1**) and $[cis\text{-Os}(\text{bpy})_2(\text{CN})_2\text{Mn}(\text{L})_2][\text{PF}_6]_2[\text{ClO}_4]_2$ (**2**) were prepared in a straightforward manner by reaction of Mn(II), Ligand **L** with $cis\text{-M}(\text{bpy})_2(\text{CN})_2$ (M = Fe, Os) in the presence of NH_4PF_6 . Crystals suitable for single-crystal X-ray diffraction analysis for **1** and **2** were obtained by slowly diffusing diethyl-ether into the DMF solution of the white precipitate at room temperature. Also both complexes **1** and **2** were characterized by IR, electronic absorption spectroscopy, elemental analysis and single-crystal X-ray diffraction analysis.

The cyanide stretching frequencies data for compounds **1** and **2**, and their precursors were listed in Table 3. The ν_{CN} of cyanide-bridged complexes of 2091 cm^{-1} for **1**, and 2070 and 2053 cm^{-1} for **2** are higher than those of their precursors, this could be attributed to both kinematical coupling occurring when a second metal is attached to the CN unit and the fact that the cyanide N donated electron density from an anti-bonding molecular orbital to the Mn(II) centre, thereby increasing the CN force constant[55, 56]. The strong peak at about 841 cm^{-1} for complexes **1** and **2** can be attributed to the stretching vibration of PF_6^- .

Table 3. Data of Cyanide Stretching Frequencies and Electronic Absorption Spectra for the Related Complexes

Compound	ν_{CN} (cm^{-1})	λ_{max} , nm(ϵ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)
<i>cis</i> -Fe(bpy) ₂ (CN) ₂ ·3H ₂ O	2069, 2079 [57, 58]	382 (6200), 590 (6280)
<i>cis</i> -Os(bpy) ₂ (CN) ₂ ·7H ₂ O	2040, 2057	348(11791), 382 (11543), 458 (10665), 506 (13000), 650 (3370)
1	2091	359 (15240), 524 (14731)
2	2070, 2053	346 (17176), 416(17477), 450 (19525), 579 (5002)

3.2 Description of the crystal structures

The molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively. Both complexes **1** and **2** crystallize in a monoclinic space groups $P2_1/n$. Compound **1** is comprised of one tetranuclear [*cis*-Fe(bpy)₂(CN)₂Mn(L)]₂⁴⁺ cation and four PF_6^- anions, and compound **2** is comprised of one tetranuclear [*cis*-Os(bpy)₂(CN)₂Mn(L)]₂⁴⁺ cation, two ClO_4^- anions and two PF_6^- anions. The tetranuclear [*cis*-M(bpy)₂(CN)₂Mn(L)]₂⁴⁺ (M = Fe, Os) cation is composed of two $[\text{M}(\text{bpy})_2]^{2+}$ and two $[\text{Mn}(\text{L})]^{2+}$ centers alternately bridged by four CN⁻ groups with the carbon atoms coordinated to the M^{II} ions in $[\text{M}(\text{bpy})_2]^{2+}$. The M^{II} ions adopt distorted $[\text{MN}_4\text{C}_2]$ octahedral coordination, in which four of the coordination sites are

occupied by nitrogen atoms from two bpy ligands, and the two remaining *cis*- positions are coordinated by carbon atoms from the cyanide groups. The Mn^{2+} ions also adopt distorted $[\text{MnN}_6]$ octahedral coordination geometry, in which four coordination sites are occupied by four nitrogen atoms from **L**, and the two remaining *cis* positions are coordinated by nitrogen atoms from the cyanide groups.

Figure 1 Crystal structure of complex **1**. Hydrogen atoms and PF_6^- anions have been omitted for clarity.

Figure 2. Crystal structure of complex **2**. Hydrogen atoms, ClO_4^- and PF_6^- anions have been omitted for clarity.

The M-C(CN) distances increase from **1** (1.890(3)-1.895(3) Å) to **2** (1.977(7)-1.980(6) Å), and

also the M-N(bpy) distances increase from **1** (1.943(3)-2.007(3) Å) to **2** (2.055(8)-2.137(8) Å).

This behavior can be contributed to the larger metallic radii of Os^{II} compared to that of Fe^{II}. The bond angles of N≡C-Fe in **1** are nearly linear with the angles of 175.8(3)° (N1≡C1-Fe1) and 171.1(3)° (N2≡C2-Fe1). Unlike the angles of N≡C-Fe, the bond angles of C≡N-Mn in **1** deviate significantly from linearity with the angles of 152.1(3)° (C1≡N1-Mn1) and 148.1(3)° (C2≡N2-Mn1). The angle of C1-Fe1-C2 is 93.12(13)°, and the angle of N2-Mn1-N1 is 96.39(11)°.

These similar behaviors can also be found in compound **2**, as listed in table 2 in detail.

The neighbouring M^{II}...Mn^{II} distances are 4.935 and 5.028 Å for **1**, and 4.988 and 5.045 Å for **2**.

The shortest intramolecular Mn^{II}...Mn^{II} separations are 7.403 Å (**1**) and 7.457 Å (**2**), respectively.

Whereas, the nearest intermolecular Mn^{II}...Mn^{II} distances are 9.347 Å (**1**) and 9.488 Å (**2**), respectively.

3.3 Electronic absorption spectroscopy

The electronic absorption spectra of complexes **1**, **2** and their precursors were measured in the CH₃CN solution at room temperature. The electronic absorption spectra of complexes **1** and **2** were presented in Figures 3 and 4, and the detailed data of them were listed in Table 3.

For the purpose of comparison, the electronic absorption spectra and the data of the related precursors Fe(bpy)₂(CN)₂·3H₂O[49, 51, 52, 59] and *cis*-Os(bpy)₂(CN)₂·7H₂O[51, 52] are also shown in Figures 3 and 4 and listed in Table 3. By comparison with their precursors, the maximum absorption wavelength at 524 nm for **1** and 450 nm for **2** can be ascribed to M^{II}→bpy (M = Fe and Os) metal to ligand charge transfer (MLCT). Furthermore, it can be seen that the maximum absorption band (Fe^{II}→bpy MLCT) is blue-shifted from the precursor *cis*-Fe(bpy)₂(CN)₂ (590 nm) to complex **1** (567 nm). This shift can be interpreted

by an increase in $d\pi(\text{Fe}) \rightarrow \pi^*(\text{bpy})$ back bonding and a concomitant decrease in $\sigma(\text{Fe}) \rightarrow \sigma(\text{bpy})$ bonding upon forming Fe-CN-Mn.[60, 61] Such blue-shifted behavior could also be observed in complex **2**. The band at λ_{max} of 579 nm in **2** may be assigned to $^3\text{MLCT}$ transition, being blue-shifted by 71 nm with respect to 650 nm of *cis*-Os^{II}(bpy)₂(CN)₂[41].

Figure 3. Electronic absorption spectra of related precursors and **1** in CH₃CN solution.

Figure 4. Electronic absorption spectra of related precursors and **2** in CH₃CN solution.

3.4 Magnetic properties

To investigate whether there exists the metal-metal interaction between distant Mn^{II} ions across the diamagnetic NCM(bpy)₂CN bridge, magnetic properties of complexes **1** and **2** were measured

and analyzed. The variable-temperature magnetic susceptibilities of complexes **1** and **2** were performed on polycrystalline samples in the temperature range of 2-300 K under an external magnetic field of 1000 Oe using a SQUID magnetometer (Figures 5 and 6). The $\chi_M T$ values at 300 K are 8.84 cm³ K mol⁻¹ for **1** and 8.78 cm³ K mol⁻¹ for **2**, which are consistent with the spin-only value of 8.75 cm³ K mol⁻¹ expected for the two uncoupled HS Mn^{II} and two diamagnetic LS M^{II} ions ($S_{Mn} = 5/2$, $S_M = 0$, $g = 2.0$). Upon cooling, the $\chi_M T$ values of **1** and **2** keep almost constant until 8.99 cm³ K mol⁻¹ at 9 K for **1** and 8.60 cm³ K mol⁻¹ at 16 K for **2**, then sharply increased to 9.89 cm³ K mol⁻¹ for **1** at 2 K, and decreased to 7.77 cm³ K mol⁻¹ for **2** at 2 K. The low temperature magnetic behaviors of **1** and **2** may be due to the zero-field splitting of Mn(II) ions and magnetic interactions between the Mn(II) ions mediated by the diamagnetic NCM(bpy)₂CN bridge, which are expected to be very weak. The magnetic properties of **1** and **2** were fitted by the Curie-Weiss law, $\chi_M = C/(T - \theta)$. The values of the best fitting for all the experiment points leading to $C = 8.70$ cm³ K mol⁻¹ and $\theta = 0.23$ K for **1**, and $C = 8.61$ cm³ K mol⁻¹ and $\theta = -0.22$ K for **2**. The Weiss constants, together with the magnetic behaviors, indicate a weak ferromagnetic coupling for complex **1**, and a weak anti-ferromagnetic coupling for complex **2**. The different magnetic properties of **1** and **2** might mainly result from their angle difference in the Mn^{III}-N≡C-M^{II}-C≡N-Mn^{III} pathway, because the magnetic properties of M1-L-M2 depends on the angle of M1-L-M2.[62] It can be found that C1≡N1-Mn1 in **1** (152.1(3)°) is obviously larger than in **2** (143.3(6)°). The similar magnetic phenomenon was also observed in the isostructural Fe and Os complexes[41]. In our previous work[47], it has also been demonstrated that for the magnetic superexchange between paramagnetic Fe(III) ions mediated by the Fe^{III}-N≡C-M^{II}-C≡N-Fe^{III} pathway involving the diamagnetic LS-M(II) centers, the magnetic coupling between

paramagnetic Fe(III) ions are related to the shape of $\text{Fe}^{\text{III}}\text{-N}\equiv\text{C-M}^{\text{II}}\text{-C}\equiv\text{N-Fe}^{\text{III}}$.

In order to quantify the magnetic coupling interaction (J) between Mn(II) ions for complexes **1** and **2**, the magnetic susceptibility data were fitted using the following equation with $\mathbf{H} = -J \mathbf{S}_A \cdot \mathbf{S}_B + (\mathbf{S}_A \cdot \mathbf{g}_A + \mathbf{S}_B \cdot \mathbf{g}_B) \mathbf{H}$: [63] $\chi = (2Ng^2\beta^2/kT) \times (e^x + 5e^{3x} + 14e^{6x} + 30e^{10x} + 55e^{15x}) / (1 + 3e^x + 5e^{3x} + 7e^{6x} + 9e^{10x} + 11e^{15x})$ with $x = J/kT$, where all symbols have their usual meaning. The best fit values obtained by the above equation are $J = 0.037 \text{ cm}^{-1}$, $g = 2.01$ and $R = 1.9 \times 10^{-3}$ for complex **1** and $J = -0.062 \text{ cm}^{-1}$, $g = 2.00$, and $R = 1.6 \times 10^{-3}$ for complex **2**.

Figure 5. Magnetic behavior of complex **1** as measured in an applied field of 1000 Oe using a SQUID magnetometer. Fitting (green line) on χ_M vs T (triangle) and fitting (red line) on $\chi_M T$ vs T (circle) of complex **1** in the polycrystalline samples.

Figure 6. Magnetic behavior of complex **2** as measured in an applied field of 1000 Oe using a SQUID magnetometer. Fitting (green line) on χ_M vs T (triangle) and fitting (red line) on $\chi_M T$ vs T

(circle) of complex **2** in the polycrystalline samples.

By comparison with the magnetic properties of the cyanide-bridged complexes reported by us[42, 46, 47], the magnetic interaction between paramagnetic Mn^{II} ions across the diamagnetic cyanidometal bridge is very weak in complexes **1** and **2**.

Conclusions

In summary, two tetra-nuclear cyanide-bridged square heterometallic complexes $[\text{cis-Fe}(\text{bpy})_2(\text{CN})_2\text{Mn}(\text{L})]_2[\text{PF}_6]_4$ (**1**) and $[\text{cis-Os}(\text{bpy})_2(\text{CN})_2\text{Mn}(\text{L})]_2[\text{PF}_6]_2[\text{ClO}_4]_2$ (**2**) were synthesized and fully characterized by IR, electronic absorption spectroscopy, elemental analysis and single-crystal X-ray diffraction analysis. Temperature-dependent magnetic properties of complexes **1** and **2** reveal the presence of the very weak magnetic interaction between distant Mn^{II} ions across the diamagnetic *cis*- $\text{NCM}^{\text{II}}(\text{bpy})_2\text{CN}$ -bridge.

Appendix A. Supplementary data

CCDC-1428533 (**1**) and CCDC-1428534 (**2**) contain the supplementary crystallographic data, related bond lengths and angles for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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