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Chlorido-Bridged Mn^{II} Schiff-Base Complex with Ferromagnetic Exchange Interactions

Chuan-Min Qi,[a] Xu-Xia Sun,[a] Song Gao,[b] Shu-Lan Ma,*[a] Da-Qiang Yuan,[c] Cui-Hong Fan,[a] Hai-Bo Huang,[a] and Wen-Xiang Zhu[a]

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The preparation, crystal structure, and magnetic properties of the μ-Cl-bridged dinuclear complex [Mn(HL)(μ-Cl)Cl]$_2$ (**1**) with the Schiff-base ligand HL, 2-methyl-6-[(pyridine-2-ylmethylene)amino]phenol, is reported. Structural studies show that **1** is binuclear with a pair of chlorine atoms bridging the manganese atoms in a central Mn_2Cl_2 plane, the intramolecular Mn···Mn separation being 3.694 Å. Each manganese atom in **1** is six-coordinate with two nitrogen atoms (one imine nitrogen and one pyridine nitrogen) and one phenolic oxygen from the neutral tridentate ligand, and three chlorine atoms (one terminal and two bridging) building an elongated octahedral environment. The two octahedra adopt the unique geometry sharing an equatorial-to-axial edge with parallel equatorial planes. The hydrogen bonds between the coordinated Cl^- anions and hydroxy groups connect the dimeric coordinated units together forming a one-dimensional chain. Variable temperature susceptibility measurements in the temperature range of 2.0–300 K reveal a ferromagnetic coupling (J = +0.94 cm^{-1}) in the dimer via the double chlorido bridge, and a weak antiferromagnetic coupling (zJ' = –0.036 cm^{-1}) between the dimers through the intermolecular hydrogen bonding. A comparison of the magnetic coupling of **1** with other structurally similar Mn(μ-Cl)$_2$-Mn compounds is discussed in detail. Complex **1** may provide useful information for the magneto-structural correlations of this kind of compounds.

Introduction

The preparation and magnetic properties of discrete polynuclear molecules and coordination polymers of paramagnetic metal complexes are of considerable interest to the field of molecular magnetism.[1] In particular, the coordination chemistry of manganese has received a great deal of attention because of the variable structures of manganese complexes and the possibility of magnetic coupling interaction.[2] The magnetic behavior of Mn^{II} polymers is dependent on the bridging and terminal ligands. Most magnetic studies on these Mn^{II} polymers are relative to those with bridging ligands, such as azide,[3] dicyanamide,[4] and carboxylate.[5] Ferromagnetic exchange coupling among these Mn^{II} compounds is rather unusual. This kind of magnetic interaction has been found in Mn^{II} dinuclear complexes and polymers with end on bridging azido,[3,6] Mn^{II} dinuclear complexes with diazine and some phenoxido bridging ligands.[7] Magnetically active chlorido-bridged systems are well-known in general, but relatively few investigations of the structure and magnetic properties of chlorido-bridged compounds have been carried out.[8] The angular dependence of the strength and nature of the magnetic coupling in M(μ-X)M systems was studied in detail for Cu^{II} and Cr^{III} systems,[1a,9] but the paucity of magneto-structural studies with dichlorido-bridged Mn^{II} dimers precludes us to go further. In order to check the correlation between the angle at the bridging chlorine atom and the nature and value of magnetic coupling in Mn^{II} compounds as well as to investigate the influence of additional structural factors, many more examples are needed. In this paper, we report the structural and magnetic study of the new dichlorido-bridged Mn^{II} dinuclear complex [Mn(HL)(μ-Cl)Cl]$_2$ (**1**) with the tridentate Schiff-base ligand. We will see that this six-coordinate Mn^{II} dimer presents unusual ferromagnetic interactions. To establish magneto/structural correlations of Mn^{II} compounds with bis(μ-chlorido) bridges, the magnetic properties of **1** were also compared to those of four structurally similar dimers, [MnCl(μ-Cl)(bpea)]$_2$ (**2**), [Mn(biz)$_2$-(μ-Cl)]$_2$Cl$_2$ (**3**), [Mn(mpbpa)Cl(μ-Cl)]$_2$ (**4**) and [Mn(dpp)-Cl(μ-Cl)(H$_2$O)]$_2$ (**5**),[8] and two one-dimensional bis(μ-chlorido) Mn^{II} complexes [Mn(μ-Cl)$_2$(bpy)]$_n$ (**6**) and [Mn(μ-Cl)$_2$(mppma)]$_n$ (**7**).[10]

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[a] College of Chemistry, Beijing Normal University,
Beijing, 100875 China
Fax: +86-10-64463640
E-mail: mashulan@263.net
[b] State Key Laboratory of Rare Earth Materials Chemistry and Application, College of Chemistry and Molecular Engineering, Peking University,
Beijing, 100871 China
[c] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences,
Fuzhou, Fujian, 350002 China

Results and Discussion

IR and UV/Vis Spectroscopy

The IR Spectra of Schiff-base ligand HL and complex **1** provide information about the metal–ligand bonding. The strong absorption band at 1624 cm^{-1} in ligand HL is assigned to the azomethine group, ν(C=N).[11] The band is shifted to lower wavenumbers at 1594 cm^{-1} in the complex, which can be attributed to the coordination of the C=N nitrogen atom to metal ions. In addition, the absorption band at 1582 cm^{-1} assigned to the pyridine group of the ligand is shifted to 1562 cm^{-1}, suggesting that the coordination of the pyridine nitrogen atom group to metal ions.[12]

The UV-visible spectroscopic data for ligand HL and the complex were studied in MeOH. Schiff-base molecule HL exhibits three maxima centered at 289, 361, and 442 nm. Complex **1** exhibits three maxima centered at 240, 349, and 474 nm. The absorption bands at 200–400 nm in the complex may correspond to ligand-centered (LC) π–π* transitions, while the strong band in the range greater than 400 nm can be ascribed to the ligand-to-metal charge transfer (LMCT) transitions.[13]

Description of the Structure

Selected bond lengths and angles of **1** are summarized in Table 1. The crystal structure of **1** consists of centrosymmetric double chlorido-bridged [Mn(HL)(μ-Cl)Cl]$_2$ dimeric units (Figure 1). One phenolic oxygen O1, one imine nitrogen N1, one pyridine nitrogen N2 from the tridentate neutral ligand, one terminal Cl1, and two bridging Cl$^-$ anions Cl2 and Cl2A (–*x* + 1, –*y* + 1, –*z*) are coordinated to one Mn^{II} ion in an elongated octahedral geometry. The best equatorial plane in the octahedron is defined by O1, N1, N2, and Cl2A set of atoms with the mean deviation of 0.0085 Å, the manganese atom being 0.1168 Å out of this mean plane. The terminal Cl1 atom occupies an axial position *trans* to the Cl2 bridge with a largest bond angle of 175.01° for Cl1–Mn1–Cl2, and a significant axial elongation (2.482 Å for Mn1–Cl1 and 2.606 Å for Mn1–Cl2) are also observed. The two small bite angles subtended at the manganese atom by the chelating ligand (69.94° for O1–Mn1–N1 and 72.92° for N1–Mn1–N2) may be considered the main reason for the distortion of the metal coordination sphere.

The Mn–N$_{\text{imine}}$, Mn–N$_{\text{py}}$ (py = pyridine), and Mn–O$_{\text{phenol}}$ distances are 2.239, 2.279, and 2.313 Å, respectively. The distance of Mn–N$_{\text{imine}}$ is close to those noted for other Mn^{II} Schiff-base complexes.[14] The M–N$_{\text{py}}$ distance is longer than M–N$_{\text{imine}}$, which is comparable to other Mn^{II} Schiff-base complexes.[14c,15]

Table 1. Selected bond lengths [Å] and bond angles [°] for complex **1**.

Mn1–O1	2.313(2)	Mn1–N1	2.239(2)
Mn1–N2	2.279(2)	Mn1–Cl1	2.4816(10)
Mn1–Cl2	2.6062(10)	Mn1–Cl2 #1	2.4511(9)
Mn1–Mn1 #1[a]	3.694		
O1–Mn1–N1	69.94(8)	O1–Mn1–N2	142.70(8)
O1–Mn1–Cl1	90.55(6)	O1–Mn1–Cl2	84.71(6)
O1–Mn1–Cl2 #1	116.70(6)	N1–Mn1–N2	72.92(9)
N1–Mn1–Cl1	91.78(6)	N1–Mn1–Cl2	88.07(6)
N1–Mn1–Cl2 #1	170.71(7)	N2–Mn1–Cl1	93.93(7)
N2–Mn1–Cl2	90.80(6)	N2–Mn1–Cl2 #1	99.84(7)
Cl1–Mn1–Cl2	175.01(3)	Cl1–Mn1–Cl2 #1	94.56(3)
Cl2–Mn1–Cl2 #1	86.20(3)	Mn1–Cl2–Mn1 #1	93.80(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 –*x* + 1, –*y* + 1, –*z*.

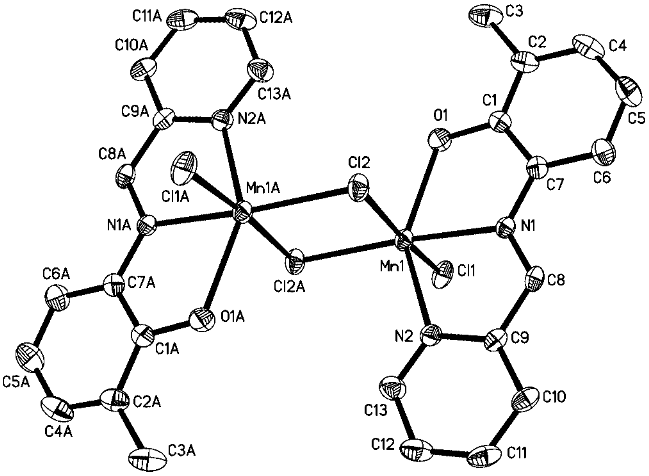


Figure 1. Molecular structure of complex **1** (thermal ellipsoids at 30% probability).

The bridging Mn$_2$Cl$_2$ unit is constrained to be planar by the presence of the crystallographic inversion center. This Mn$_2$Cl$_2$ plane is practically orthogonal with the above equatorial plane O1/N1/N2/Cl2A in the octahedron, the value of the dihedral angle between both planes being 86.6°. The Mn–Cl–Mn angle of 93.80° and the different Mn–Cl distances of 2.451 and 2.606 Å show that the Mn$_2$Cl$_2$ core is considerably distorted from an ideal square. The two Mn–Cl bonds within the Mn$_2$Cl$_2$ core lie within the typical range for bridged Mn^{II} chloride atoms (2.31–2.61 Å),[8c,8d,16] being longer than those terminal Mn^{II}–chlorido bonds (2.27–2.37 Å)[17] observed in other complexes. The two Mn–Cl$_{\text{bridge}}$ bonds in **1** are significantly different, and the terminal Mn–Cl bond (2.482 Å), essentially coplanar with the Mn$_2$Cl$_2$ core, is between the Mn–Cl$_{\text{bridge}}$ bonds, which is divergent from other di-μ-chlorido Mn^{II} complexes containing longer Mn–Cl$_{\text{bridge}}$ bonds than Mn–Cl$_{\text{terminal}}$ bonds.[8a,18] The intramolecular Mn–Mn distance of 3.694 Å in **1** is shorter than other hexacoordinate dinuclear Mn^{II} compounds with chlorido and nitrogen ligands (3.74–3.85 Å),[8a,8c,8d,18a] which points to a strong effect of the chlorido bridges in **1**. The whole Schiff-base molecule (N1/N2/O1/C1–C13) is merely an approximate plane with a deviation of 0.0695 Å. This distortion from planarity may be due to intermolecular hydrogen bonding interactions. There exist intermolecular hydrogen bonds in **1**. The hydroxy group O1–H1 of the dimer is hydrogen bonded to the Cl1B anion (–*x*, –*y* + 1, –*z*) of one adjacent dimer and forms O1–H1···Cl1B (O1···ClB 3.004 Å, H1···ClB 2.198 Å, and the O1–H1···Cl1B 157.83°), and the Cl1 anion of the present dimer forms a hydrogen bond Cl1···H1B–O1B (–x, –y + 1, –z) with the hydroxy group of the adjacent unit. The hydroxy group O1A–H1A of the present dimer is again hydrogen-bonded to Cl1D (x + 1, y, z) of another adjacent dimer and forms O1A–H1A···Cl1D, and at the same time the Cl1A anion forms a hydrogen bond Cl1A···H1C–O1C (x + 1, y, z) with the hydroxy of the adjacent unit. As a result, the hydrogen bonds between coordinated Cl^- anions and hydroxy groups tie the coordinated dimeric units together forming a one-dimensional zig–zag chain (Figure 2). In the chain, the shortest interdimer manganese–manganese distance is 5.523 Å for Mn1–Mn1B (–x, –y + 1, –z).

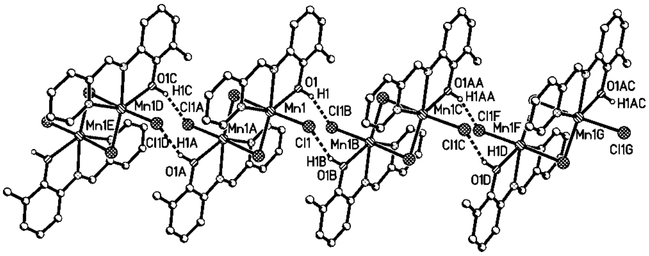


Figure 2. The one-dimensional hydrogen bond chain extending along the a axis of **1** (some hydrogen atoms are omitted for clarity).

Magnetic Properties

Variable temperature magnetic susceptibility on **1** was measured in the range 2.0–300 K (Figure 3). At room temperature, the χ_mT value for the dinuclear unity is 8.73 $cm^3 mol^{-1} K$, a value which is as expected for two independent spins S = 5/2 (8.75 $cm^3 mol^{-1} K$). Upon cooling from room temperature, χ_mT increases smoothly at first until around 80 K, below this temperature it increases sharply to reach a maximum of 11.24 $cm^3 mol^{-1} K$ at 6.0 K and then decreases rapidly to 9.70 $cm^3 mol^{-1} K$ at 2.0 K. The χ_m^{-1} versus T plot is essentially linear, and least-squares fitting of the data to the Curie–Weiss law gave C = 8.72 $cm^3 mol^{-1} K$ and θ = +1.74 K. The increase in χ_mT upon cooling and the positive Weiss constant indicates that there exists a ferromagnetic coupling between two Mn^{II} centers in the dimer. The rapid decrease in χ_mT at lower temperatures is probably due to the weak antiferromagnetic interdimer interaction.[19] This latter contribution is also supported by the field dependence of the magnetization recorded at 2 K (Figure 4) with a magnetization which tends to a saturation value of 9.46 Nβ, slightly below the expected saturation value of 10.0 Nβ for two S = 5/2 spins without interactions.[20]

Keeping in mind the structure of **1**, the magnetic data were fitted through Equation (1),[8b,21] which considers both the intradimer and interdimer interactions. The additional coupling parameter, zJ', was added to take into account the magnetic behavior at low temperature as a molecular field approximation.[22]

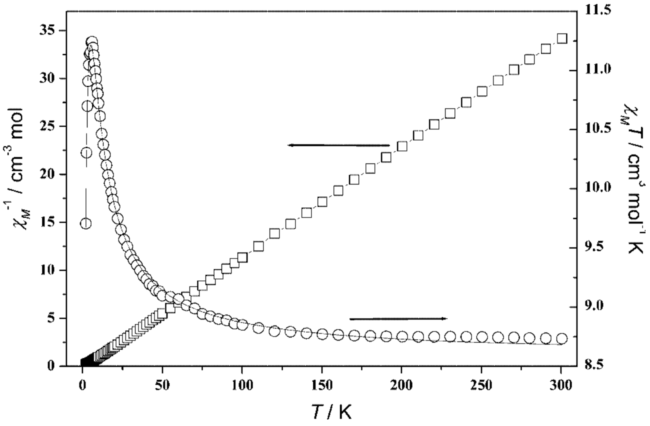


Figure 3. The plot of temperature dependence of χ_m^{-1} (□) and χ_mT (○) of **1** measured at 1000 Oe. The solid line represents the best fit of the experimental data as discussed in the text.

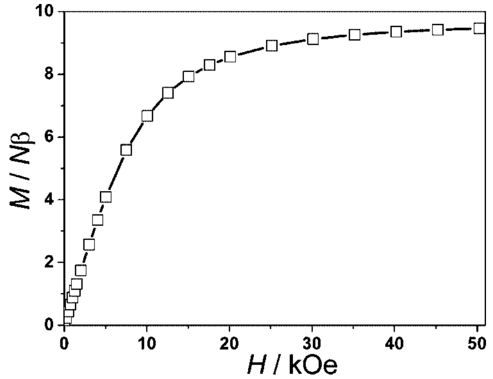


Figure 4. Magnetization vs. field up to H = 50 kOe at 2.0 K. (The solid line is only a guide for the eye and does not indicate fitting).

$$\chi_M = \frac{\chi_t}{1-(2zJ'/Ng^2\beta^2)\chi_t} \qquad (1)$$

where

$$\chi_t = \frac{2Ng^2\beta^2}{kT} \times \frac{55+30\exp(5x)+14\exp(9x)+5\exp(12x)+\exp(14x)}{11+9\exp(5x)+7\exp(9x)+5\exp(12x)+3\exp(14x)+\exp(15x)}$$

with $\quad x = -J/kT$

The best fitting of the data in the temperature range 2–300 K leads to the parameters g = 1.98, J = +0.94 cm^{-1}, zJ' = –0.036 cm^{-1}. The reliability factor R, defined as $R(\chi_mT) = \Sigma(\chi_mT_{obs}-\chi_mT_{calc})^2/\Sigma(\chi_mT_{obs})^2$, is equal to 9.97×10^{-6}. The calculated data curve (solid line in Figure 3) matches the experimental magnetic data very well. The results indicate magnetic exchange interactions should mainly pass through the double μ-Cl bridge pathway, which exhibits a ferromagnetic coupling interaction via the double chlorido bridges. The smaller negative zJ' value shows that there exists a weak antiferromagnetic interaction between the Mn^{II} dimers through the intermolecular hydrogen bonding.

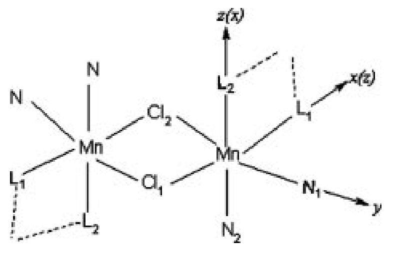
Ferromagnetic interactions between two S = 5/2 Mn^{II} centers via chlorido bridges is precedented but has not been studied in detail. A spin dimer of S = 5/2 Mn^{II} is expected to exhibit J coupling of at least 25 times less than a spin dimer of S = 1/2 Cu^{II},[23] and thus the values of J of the dichlorido-bridged manganese(II) complexes are usually small as listed in Table 2.

Table 2. Structural parameters and magnetic coupling constants for Mn^{II} complexes with a $[Mn_2(\mu\text{-}Cl)_2]^{2+}$ unit.

Dinuclear complexes[a]	[b]	$a_{Mn-Cl-Mn}$ [°]	d_{Mn-Mn} [Å]	d_{Mn-Cl} [Å]	J [cm^{-1}]	Geometry	$\Sigma\Delta_i^2$	Ref.
$[Mn(HL)(\mu\text{-}Cl)Cl]_2$ (**1**)	L_1 = Cl	93.8	3.694	2.61	+0.94	I		this work
	L_2 = O			2.45				
$[MnCl(\mu\text{-}Cl)(bpea)]_2$ (**2**)	L_1 = N	95.7	3.786	2.57	+0.34	II	0.101	[8a]
	L_2 = Cl			2.54				
$[Mn(biz)_2(\mu\text{-}Cl)]_2Cl_2$ (**3**)	L_1 = N	93.5	3.740	2.57	+0.33	II	0.181	[8c]
	L_2 = N			2.56				
$[Mn(mpbpa)Cl(\mu\text{-}Cl)]_2$ (**4**)	L_1 = N	96.4	3.850	2.60	+0.55	II	0.082	[8d]
	L_2 = Cl			2.57				
$[Mn(dpp)Cl(\mu\text{-}Cl)(H_2O)]_2$ (**5**)	L_1 = Cl	95.6	3.805	2.61	+0.11	I	0.021	[8b]
	L_2 = O			2.52				
One-dimensional complexes								
$[Mn(\mu\text{-}Cl)_2(bpy)]_n$ (**6**)	L_1 = Cl	96.38	3.835	2.66	+0.19	I	0.021	[10a]
	L_2 = Cl			2.48				
$[Mn(\mu\text{-}Cl)_2(mppma)]_n$ (**7**)	L_1 = Cl	95.4[c]	3.790[c]	2.59[c]	–0.25	II	0.063	[10b]
	L_2 = Cl			2.54[c]				

[a] Abbreviations: HL = 2-methyl-6-[(pyridine-2-ylmethylene)amino]phenol; bpea = *N*,*N*-[bis(2-pyridylmethyl)ethylamine]; biz = 2,2′-biimidazoline; mpbpa, *N*-(3-methoxypropyl)-*N*,*N*-bis(pyridin-2-ylmethyl)amine; dpp = 2,3-bis(2-pyridyl)pyrazine; bpy = 2,2′-bipyridine; mppma = *N*-(3-methoxypropyl)-*N*-(pyridin-2-ylmethyl)amine. [b] See Scheme 1. [c] Average values of the angles and the distances in the two nonequivalent $[Mn_2(\mu\text{-}Cl)_2]^{2+}$.

Many one-dimensional six-coordinate bis(μ-chlorido)-Mn^{II} polymers are reported and most of them show antiferromagnetic coupling.[10b,24] There are few bis(μ-chlorido)-Mn^{II} dinuclear complexes reported and they exhibit ferromagnetic coupling[8] or antiferromagnetic interaction.[25] Table 2 summarizes some structural parameters and magnetic coupling constants for the dinuclear and one-dimensional dichlorido-bridged complexes with similar structures of **1**. With the aim to compare the magnetic properties of these compounds, the one-dimensional systems have been considered as dinuclear complexes (Scheme 1). In all cases, a rectangular core is observed with two distinct Mn–Cl distances. In a *trans* disposition to one chlorido bridge (with the short Mn–Cl distance), there is a N-ligand, while *trans* to the other chlorido bridge (with long Mn–Cl distance) the L1 ligand could be Cl (for **1**, **5**, **6**, and **7**) or N (for **2**, **3**, and **4**) (Scheme 1). The other two positions of the octahedron are occupied by a N-ligand and by an L2 ligand. For compounds **2**, **4**, **6**, and **7** this ligand (L2) is Cl, while for **3** it is an N-ligand, and for **1** and **5** it is an O-ligand. The different kinds of ligands around the Mn^{II} ions give rise to different distortions in the coordination polyhedron.



Scheme 1.

There are two types of geometries that have been characterized in the literatures: geometry I has two octahedra sharing an equatorial-to-axial edge with parallel equatorial planes, and geometry II has two octahedra sharing an equatorial edge with coplanar equatorial planes. For compounds **1**, **5**, and **6** with well-differentiated $Mn–Cl_{bridge}$ distances (Table 2), geometry I is often observed, while for compounds as **2**, **3**, **4**, and **7** containing near $Mn–Cl_{bridge}$ values, geometry II is formed. Extended Hückel calculations with the CACAO program for the six complexes (**2**–**7**) showed that for axially elongated compound **6**, the $d_{x^2-y^2}$ orbital of the manganese ions is perpendicular to the Mn_2Cl_2 plane and points to one chlorido bridge while the d_{z^2} orbital points to the other bridge. For other compounds with smaller distortion on the octahedron the $d_{x^2-y^2}$ orbitals are in the Mn_2Cl_2 plane, and the magnetic interaction may be sensitive to the Mn–Cl–Mn angle.[10a] The different magnetic interaction for the two one-dimensional complexes **6** and **7** with similar structure could be attributed to the major axial elongation on the octahedron present in **6**. Important elongation of the octahedron in our complex **1** is also observed as **6**, and the two $d_{x^2-y^2}$ orbitals of the Mn^{II} ions of **1** may be parallel as in **6**. The $d_{x^2-y^2} \pm d_{x^2-y^2}$ could be quite degenerated, and thus the antiferromagnetic contribution, depending on Δ_i gaps and the overlap through the bridging ligands, as being shown $J_{AF} \propto \Sigma\Delta_i^2$, may be smaller, which agrees with the ferromagnetic behavior observed in this case (J = +0.94 cm^{-1}). From Table 2 we can see that for the complexes with geometry I, the values of $\Sigma\Delta_i^2$ are minor, and for those with geometry II, major values of $\Sigma\Delta_i^2$ are often shown.[10a] There should be certain correlation among the coordination geometry, the disposition of $d_{x^2-y^2}$ orbital of the metal ions, the value of $\Sigma\Delta_i^2$, and the magnetic interaction.

Another complex **5**[8b] also adopts geometry I, but no important elongation on the octahedron is observed as **6**, and the different disposition of $d_{x^2-y^2}$ orbitals may result in its small positive value of *J*.

The sign and magnitude of the coupling constant for $Cu(\mu\text{-}Cl)_2Cu$ dimers depend mainly on the Cu–Cl–Cu bridging angle, the Cu–Cl distance, the nature of the terminal ligands, and the coordination geometry.[26] An important result of the DFT study is that the presence of N-donor terminal ligands seems to favor the ferromagnetic coupling, whereas replacement by halide anions results in the antiferromagnetic behavior.[26b] These results could also explain the magnetic interaction of these chlorido-bridged Mn^{II} complexes. A major value of $\sum\Delta_i^2$ was found for **3** relative to its structurally similar complexes **2** and **4**, and a minor ferromagnetic interaction should be attended. Nevertheless, the major number of N-terminal ligands and the minor Mn–Cl–Mn angle of **3** relative to other compounds may contribute its not small, positive *J* value.

Complex **1** contains quite more differentiated Mn–Cl_{bridge} distances and an obvious axial elongation on the octahedron, which induce the rare octahedral geometry I with parallel equatorial planes and determine the unique disposition of $d_{x^2-y^2}$ orbital of the two Mn^{II} ions. The peculiar geometry and the smallest Mn–Cl–Mn angle and shorter Mn–Mn distance of **1** compared with other compounds may induce its strongest ferromagnetic behavior.

The interesting structure and the novel ferromagnetic behavior of complex **1** might provide useful information for the magneto-structural correlations for dichlorido-bridged Mn^{II} systems in the future. With continued research efforts designed to improve theoretical models and to obtain a greater number of experimental examples, the nature of the relationship between the structural properties and the exchange-coupling constant for these systems can be refined.

Conclusions

We prepared and characterized dichlorido-bridged Mn^{II} complex **1** with ferromagnetic exchange interactions. Complex **1** is binuclear with a pair of chlorine atoms bridging the manganese atoms in a central Mn_2Cl_2 plane, the intramolecular Mn···Mn separation being 3.694 Å. The hydrogen bonds between the coordinated Cl^- anions and hydroxy groups tie the dimeric units together forming a one-dimensional chain. There are two well-differentiated Mn–Cl_{bridge} bonds in the Mn_2Cl_2 core and obvious axial elongation on the octahedron of the metal Mn^{II} ion. These structural features induce the geometry I of two octahedra sharing an equatorial-to-axial edge with parallel equatorial planes. This unique geometry may cause a parallel disposition of $d_{x^2-y^2}$ orbitals (and the d_{z^2} orbitals) of the Mn^{II} ions, and minor values of the antiferromagnetic contribution $\sum\Delta_i^2$ could be attended, and thus a ferromagnetic interaction is observed. The smallest Mn–Cl–Mn angle and the shorter Mn–Mn distance of **1** may also induce its maximum *J* value.

Experimental Section

General: All commercially available chemicals were of analytical grade and used as received. C, H, and N analyses were determined with an Elementar vario EL elemental analyzer. UV-visible spectra were measured with a GBC Cintra 10e UV/Vis spectrophotometer in MeOH solution. The IR spectra were recorded with a Nicolet-AVATAR 360 FTIR spectrometer using KBr pellets in the 4000–400 cm^{-1} regions. Variable-temperature magnetic susceptibility data for the crystalline sample of complex **1** was obtained in an external field of 1000 G with an Oxford Maglab 2000 system magnetometer in the 2–300 K temperature range. The susceptibilities were corrected for diamagnetism with Pascal's constants for all the constituent atoms.

Ligand HL: A mixture of pyridine-2-carbaldehyde (0.107 g, 1 mmol) and 2-amino-6-methylphenol (0.123 g, 1 mmol) was heated at reflux in anhydrous ethanol (20 mL) for 2 h. After the solvent was removed under reduced pressure, *n*-hexane (20 mL) was then added, and the mixture was heated at reflux for another 0.5 h. The reaction mixture was filtered and left to stand at room temperature and brown crystals were obtained from the filtrate after 15 min. Yield: 0.172 g, 81 %. M.p. 95–96 °C. ^1H NMR (500 MHz, DMSO): δ = 8.76 (s, 1 H, phenol-OH), 8.74 (s, 1 H, imide-H), 8.70 (d, *J* = 4.2 Hz, 1 H, pyridine-H), 8.58 (d, *J* = 7.9 Hz, 1 H, pyridine-H), 7.96 (t, *J* = 7.6 Hz, 1 H, pyridine-H), 7.50 (t, *J* = 6.3 Hz, 1 H, pyridine-H), 7.28 (d, *J* = 7.9 Hz, 1 H, Ar-H), 7.08 (d, *J* = 7.3 Hz, 1 H, Ar-H), 6.78 (t, *J* = 7.7 Hz, 1 H, Ar-H), 2.22 (s, 3 H, $-CH_3$) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3402, 3046, 2921, 1624, 1600, 1582, 1566, 1476, 1433, 1344, 1235, 1163, 1082, 1013, 991, 944, 834, 783, 742, 733, 598 cm^{-1}. UV/Vis (MeOH): λ (ε, $10^4\ M^{-1}cm^{-1}$) = 289(4.25), 361(4.92), 442(1.50) nm. $C_{13}H_{12}N_2O$ (212.10): calcd. C 73.56, H 5.70, N 13.20; found C 73.57, H 5.92, N 13.22.

$[Mn(HL)(\mu\text{-}Cl)Cl]_2$ (1): To a yellow solution of HL (0.011 g, 0.05 mmol) in CH_2Cl_2 (5 mL) was added a solution of $MnCl_2\cdot 4H_2O$ (0.010 g, 0.05 mmol) in CH_3CH_3OH (5 mL) dropwise with stirring for 1 h. The reaction mixture was filtered and left to stand at room temperature. On slow evaporation of the solution for several days, the deep red crystals of **1** suitable for X-ray analysis were collected. IR (KBr pellet): $\tilde{\nu}$ = 3420, 3052, 1594, 1562, 1481, 1373, 1324, 1272, 1209, 1173, 1112, 988, 894, 781, 748, 637,

Table 3. Crystal data and structure refinement details for complex **1**.

Empirical formula	$C_{26}H_{24}N_4O_2Cl_4Mn_2$
Formula weight	676.17
Temperature [K]	294(2)
Wavelength [Å]	0.71073
Crystal system, space group	triclinic, $P\bar{1}$
a [Å], *α* [°]	7.6610(18), 70.347(4)
b [Å], *β* [°]	9.589(2), 70.320(4)
c [Å], *γ* [°]	11.046(3), 74.992(4)
Volume [Å^3]	709.8(3)
Z, Calculated density [$g\,cm^{-3}$]	1, 1.577
Absorption coefficient [mm^{-1}]	1.297
F(000)	340
Crystal size [mm]	0.20 × 0.12 × 0.08
θ range for data collection [°]	2.04–25.01
Limiting indices	$-8 \le h \le 9$, $-10 \le h \le 11$, $-7 \le h \le 13$
Reflections collected/unique	3598/2487 [R_{int} = 0.0184]
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	2487/0/173
Goodness of fit on F^2	1.053
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0321, wR_2 = 0.0694
R indices (all data)	R_1 = 0.0572, wR_2 = 0.0836

547 cm^{-1}. UV/Vis (MeOH): λ (ε, 10^3 M^{-1}cm^{-1}) = 240(11.75), 349(7.73), 474(3.36) nm. $C_{26}H_{24}Cl_4Mn_2N_4O_2$ (676.17): calcd. C 46.14, H 3.55, N 8.28; found C 46.28, H 3.45, N 8.20.

X-ray Crystallographic Study: The crystal with dimensions $0.20 \times 0.12 \times 0.08$ mm of **1** was selected for X-ray diffraction experiments. The measurements were performed with a Bruker SMART 1000 CCD diffractometer at room temperature (293 K) with graphite monochromatized $Mo\text{-}K_{\alpha}$ radiation (λ = 0.71073 Å). Semiempirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXS-97 and SHELXL-97 programs.[27] All non-hydrogen atoms were refined with anisotropic displacement parameters and the hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinements. A summary of the crystallographic data and details of the structure refinements are listed in Table 3. CCDC-298016 contains the 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.

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