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Synthesis, crystal structures and magnetic studies on the nickel(II) and manganese(II) complexes containing the 2-pyridyl methyl ketazine

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ABSTRACT

Two double helical compounds with a general cationic structure $[\mathrm{M^{II}}_2(\mathbf{L^1})_2(\mathrm{Cl})_3]^+$ have been obtained by treatment of $\mathbf{L^1}$ ($\mathbf{L^1}$ = 2-pyridyl methyl ketazine) and hydrated $\mathrm{M^{II}Cl_2}$ in MeOH, which were isolated as a $\mathrm{PF_6^-}$ salt (M=Ni, **1**) and a $\mathrm{ClO_4^-}$ salt (M=Mn, **2**), respectively. They represent first examples of double helicates of diazine complexes containing pseudo octahedral-coordinated metal ions. Their crystal structures have been determined by X-ray crystallography and the corresponding magnetic properties have been investigated in detail.

The chemistry of hydrazone and diazine ligands is of great interest, *due* to their versatile coordination modes and complicated reactivity towards oxidation. We have previously investigated the chemistry of hydrazone in the presence of some transition metal ions such as $\mathrm{Cu^{2+}}$ and $\mathrm{Zn^{2+}}$ [1–3]. The main observation about the chemistry is the competition reactions between the oxidative coupling of primary alcohol with hydrazone to form bis(hydrazone) complexes and oxidative cyclization of hydrazone to form triazolo complexes. The different substituents on the imine function of hydrazone and the effect of metal ions towards the reactivity of hydrazone have been investigated in detail.

The coordination chemistry of diazine ligands has also attracted wide attention, *due* to the inherent helical nature from two pyridylimine units that are connected by a N—N single bond. This single bond has enough rigidity to sterically prevent the two metal binding sites from coordinating to a single metal center [4–7]. More interestingly, chiral helices will result when diazine ligands bind two metal ions with the same absolute configurations [8–12]. Yan et al. have recently reported a few chiral molecular magnets based on the diazine ligands, which exhibit stronger magnetochiral dichroism (MChD) [13,14]. So far, a number of metal compounds containing these types of ligands have been obtained and their single crystal structures have been determined by X-ray crystallography. Many of them exhibit the helical architectures. An conclusion about the helical features of these compounds could be made: metal complexes of $\mathrm{Cu^{2+}}$, $\mathrm{Ni^{2+}}$, $\mathrm{Mn^{2+}}$ and $\mathrm{Fe^{2+}}$ ions having stronger coordination preference to form octahedral geometry usually exhibit dinuclear triply helical architectures; on contrary, for d^{10} metal ions such as $\mathrm{Cu^+}$, $\mathrm{Ag^+}$ having greater coordination flexibility, their complexes usually exhibit a more diverse range of architectures [15,16]. Systematic studies have been performed to probe how different metal ions affect the architectures and the extent to which substituents attached to imine function of azine ligands can also influence the architecture adopted. However, it is surprising to note that the effect of ancillary ligands towards helical structures in these systems is much less studied [17,18]. We reasoned that if the *cis*-positions of the octahedral geometry were occupied by two ancillary ligands, the four empty positions could be coordinated by two bis-bidentate pyridylimine units and such a conformation of the two metal centers was more suitable for the construction of a dinuclear double helical complex. Herein, we intend to make a study on the effect of $\mathrm{Cl^-}$ towards helicates. Two double helical compounds with a general cationic structure $[\mathrm{M^{II}}_2(\mathbf{L^1})_2(\mathrm{Cl})_3]^+$ have been obtained by treatment of $\mathbf{L^1}$ ($\mathbf{L^1}$ = 2-pyridyl methyl ketazine, Fig. 1) and hydrated $\mathrm{M^{II}Cl_2}$ in MeOH, which were isolated as a $\mathrm{PF_6^-}$ salt (M=Ni, **1**) and a $\mathrm{ClO_4^-}$ salt (M=Mn, **2**), respectively. Their crystal structures and corresponding properties have been investigated in detail.

The reaction of $\mathbf{L^1}$ and hydrated $\mathrm{Ni^{II}Cl_2}$ with a 1:1 ratio in MeOH in the presence of excess $\mathrm{NH_4PF_6}$ gives the compound $[\mathrm{Ni^{II}}_2(\mathbf{L^1})_2(\mathrm{Cl})_3]\mathrm{PF_6}$ (**1**) as the major product [19], which is isolated as a green air-stable paramagnetic microcrystalline solid (Scheme 1). **1** is sparely soluble in alcohol, but is well soluble in $\mathrm{CH_3CN}$. Moreover, a minor product $[\mathrm{Ni^{II}}(\mathbf{L^2})_3](\mathrm{PF_6})_2$ (**2**) is also isolated as a paramagnetic red microcrystalline solid. The ligand $\mathbf{L^2}$ is *in-situ* formed from hydrolysis of $\mathbf{L^1}$. The similar hydrolytic reaction of phenyl 2-pyridyl ketone azine with $\mathrm{CuCl_2}$ has been reported previously [4b]. In the similar condition, the reaction of $\mathbf{L^1}$ and hydrated $\mathrm{Mn^{II}Cl_2}$ with a 1:1 ratio in MeOH also affords the similar product $[\mathrm{Mn^{II}}_2(\mathbf{L^1})_2(\mathrm{Cl})_3]^+$, which is isolated as $\mathrm{ClO_4^-}$ salts (**3**) [20]. However, the hydrolytic product $[\mathrm{Mn^{II}}(\mathbf{L^2})_3]^{2+}$ is not observed. All the compounds have been characterized by IR, ESI/MS and elemental analysis. IR spectrum of **1** shows

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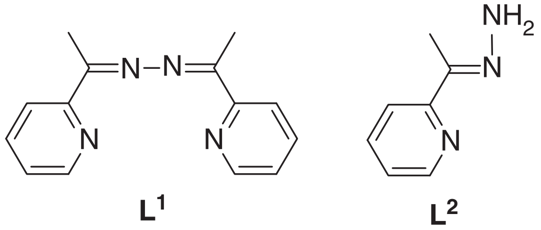
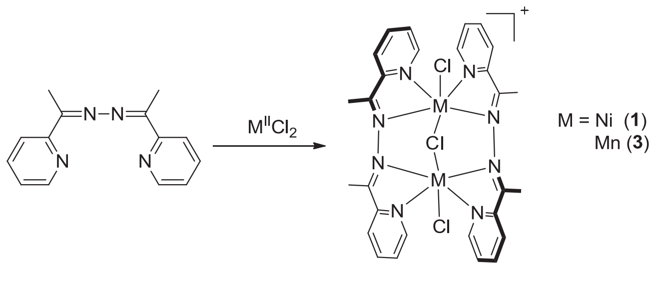


Fig. 1. Structures of ligands $\mathbf{L^1}$ and $\mathbf{L^2}$.

ν(C=N) stretch at 1589 cm^{-1} and ν(P–F) stretch at 839 cm^{-1}. ESI/MS of **1** in CH_3CN shows two predominant peaks at *m/z* 699.0 and 332.0, which are assigned to parent anion $[M]^+$ and $[M - Cl]^{2+}$, respectively. IR of **2** shows the ν(N–H) stretch at 3427, 3337 cm^{-1}, ν(C=N) stretch at 1604 cm^{-1} and ν(P–F) stretch at 840 cm^{-1}, respectively. ESI/MS of **2** in MeOH (+ mode) shows two predominant peaks at *m/z* 231.5, 608.0, which are assigned to $[M]^{2+}$ and $[M+PF_6]^+$, respectively. Compound **2** has a room-temperature magnetic moment of 2.87 μ_B (Gouy method, solid sample), which is consistent with its formulation as a high spin d^8 Ni^{II} complex in an octahedral symmetry. IR spectrum of **3** shows ν(C=N) stretch at 1592 cm^{-1} and ν(Cl–O) stretch at 1089 cm^{-1}. ESI/MS of **3** in CH_3CN shows two predominant peaks at *m/z* 691.0 and 328.0, which are assigned to parent anion $[M]^+$ and $[M–Cl]^{2+}$, respectively. The cyclic voltammogram (CV) of **3** in 0.1 M $[N^nBu_4]PF_6$ in CH_3CN displays an irreversible couple, centered at $E_{pa}=+0.94$ V (versus $Cp_2Fe^{+/0}$; Cp = cyclopentadienyl), respectively (Fig. S1). The irreversibility of the oxidation wave precludes characterization of the oxidized species by experimental methods, thus it is hard to evaluate the electronic communication of two manganese centers *via* chloride and N—N bridges. The elemental analyses of these compounds are excellent in agreement with their proposed structures.

The crystal structure of **1** has been determined by X-ray crystallography, as shown in Fig. 2 [21]. The complex crystallizes in orthorhombic *Pccn* group system. Only half of the double helicate is found in an asymmetry unit, since there is a C_2 rotation axis passing through the center of Ni1 and $Ni1^i$ (symmetry code *i*: $-x+1/2, -y+1/2, z$) atoms and the bridging Cl2 atom. Each Ni^{II} ion is chelated by four nitrogen atoms from two pyridylimine groups of two distinct $\mathbf{L^1}$ ligands and two chloride atoms to form a distorted *cis*-octahedral geometry. What interests us is how the twisting of $\mathbf{L^1}$ induces the helical nature of **1**. The pyridylimine units of $\mathbf{L^1}$ are essentially planar; however, there is substantial twisting about the central N—N bond. The dihedral angle between the two planar pyridylimine groups is 68.1º, giving rise to a twisted spiral conformation for the whole ligand. The dihedral angle of ligand $\mathbf{L^1}$ in $[Ni_2(\mathbf{L^1})_3]^{4+}$ is 72.7° [22], which is more distorted than that of **1**, since the distortion of $\mathbf{L^1}$ in **1** is relieved in part by the coordination of three Cl^- ligands. The Ni—N bond lengths are in the narrow range of 2.075(4)–2.091(4) Å, which are comparable with those in the similar compounds [5]. The terminal Ni—Cl1 bond distance is 2.352 Å, which is shorter than that of Ni—Cl2 (2.482 Å). The two Ni^{II} ions are triply linked by two N-N diazines and a chloride to form a dinuclear unit. The Ni—Cl—Ni bond angle is 89.8°, close to right angle. The acuter angle leads to closer inter-metallic separation of two Ni(II) ions with a value of 3.506(2) Å, which is shorter than that in the triply helical complex $[Ni_2(\mathbf{L^1})_3]^{4+}$ with the Ni···Ni distance of 3.683(2) Å [22].



Scheme 1. The reaction of $\mathbf{L^1}$ with hydrated $M^{II}Cl_2$ in MeOH.

Fig. 3 shows the cationic structure of **3** [23]. The asymmetric unit consists of a cationic $[Mn^{II}{}_2(\mathbf{L^1})_2Cl_3]^+$ and a ClO_4^- and two CH_3CN molecules. The complex crystallizes in monoclinic *P2₁/c* group system. The cationic structure of **3** is essentially the same to **1**; however, the presence of two CH_3CN molecules causes its departure from crystallographic C_2 symmetry. The bond parameters around the manganese(II) center are obviously different form that of **1**, possibly *due* to the diversity of their ionic radius and Pauling electronegativity. The radius of Ni^{2+} (0.72 Å) is smaller than that of Mn^{2+} (0.80 Å) so that there is a restriction of the coordination space around Ni^{2+} in comparison with Mn^{2+}. On the other hand, the Pauling electronegativity of Ni is 1.9 while that of Mn is 1.5. Thus, nickel has a stronger coordination capability than manganese. The larger ionic radius and weaker coordination capability lead to longer metal–nitrogen bond lengths. The Mn—N bond distances are in the range of 2.246(2)–2.312(2) Å, which are comparable with the similar Mn^{II} complexes [13,14]. The two terminal Mn—Cl bond lengths are 2.312(2) and 2.3810(8) Å, respectively. These bond distances are significantly shorter than the bridging Mn—Cl bond distances (2.5353(7) and 2.5764(8) Å, respectively). The Mn—Cl—Mn bond angle is 98.35(3)º and the Mn···Mn separation is 3.868 Å. The two pyridylimine units of $\mathbf{L^1}$ in **3** are not symmetry-related as that in **1**. Thus, the dihedral angles of two pyridylimine units of $\mathbf{L^1}$ in **3** are not equivalent with the values of 78.2º and 65.5º, respectively one of which is significantly more twisted than the Ni^{II} analogue. It is noteworthy to note that the cationic structures $[M^{II}{}_2(\mathbf{L^1})_2Cl_3]^+$ in **1** and **3** possess dinuclear double helical architectures. The coordination of chloride ions prevents formation of dinuclear triple-helicates, which are commonly observed in the Ni^{II} and Mn^{II} complexes containing these types of ligands. Although a number of helical structures bearing this class of ligands have been obtained, it is first time to observe that diazine complexes bearing the metal centers having stronger octahedral coordination preference exhibit dinuclear double-helicates. The ancillary ligands Cl^- play a significant role for the resulting structures. In the packing diagrams of **1** and **3**, there is no obvious π-π interactions among the pyridylimine units, possibly because the steric methyl group weaken the potential intermolecular interactions between pyridine rings [5].

Attempts to further investigate the effect of methyl group in $\mathbf{L^1}$, we also used 2-pyridyl phenyl ketazine ($\mathbf{L^3}$) instead of $\mathbf{L^1}$. In similar conditions, the reaction of hydrated $Ni^{II}Cl_2$ with $\mathbf{L^3}$ afforded $[Ni(\mathbf{L^3})_2]^{2+}$, where $\mathbf{L^3}$ acted as a tridentate ligand [5]. Moreover, the presence of Cl^- has been proved to be necessary for the double helical architectures: using $Ni^{II}(ClO_4)_2$ or $Ni(PF_6)_2$ instead of hydrated $NiCl_2$ in MeOH or CH_3CN, the reactions readily gave the triply helical complex $[Ni_2(\mathbf{L^1})_3]^{4+}$ [22] rather than $[Ni_2(\mathbf{L^1})_2(solvent)_4]^{4+}$.

The temperature dependence of the molar magnetic susceptibility of **1** was measured in the range of 2–300 K under the external magnetic field of 1 kOe (Fig. 4 (left)). The χ_MT value at room temperature is 1.88 $cm^3\ mol^{-1}$ K, which is close to the uncoupled, spin-only value of 2 $cm^3\ mol^{-1}$ K for two high spin Ni^{II} center with $S=1$. On lowering the temperature, the χ_MT value decreases slowly and reaches 1.69 $cm^3\ mol^{-1}$ K and then it decreases sharply and reaches a minimum value of 0.20 $cm^3\ mol^{-1}$ K at ~2 K. The molar magnetic susceptibility above 30 K can be fitted by Curie-Weiss law with the Curie constant $C=1.92$ $cm^3\ mol^{-1}$ K and the negative Weiss constant $\theta=-6.05$ K. The negative value of θ and the monotonic decrease of χ_MT value upon lowering the temperature suggest the presence of overall strong antiferromagnetic interaction between the two Ni^{II} centers *via* the chloride and N-N diazine bridges. The magnetization of this compound as a function of applied field at 2 K is depicted in Fig. 4 (right). At 50 kOe, the magnetization of per $[Ni^{II}{}_2]$ reaches a value of 1.06 $N\beta$, which is quite far from the expected value of 4.0 $N\beta$ for the sum of two Ni^{II} magnetic moments ($S_T=2S_{Ni}=2$; $M_S=gS_TN\beta$, assuming $g=2.0$), again suggesting the antiferromagnetic coupling between two Ni^{II} ions centers in **1**.