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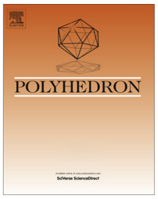

Five new pseudohalide bridged Mn(II) complexes of pyrimidine derived Schiff base ligands: Synthesis, crystal structures and magnetic properties

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ABSTRACT

Four new azide bridged dinuclear Mn(II) complexes $[Mn(L_1)(\mu_{1,1}\text{-}N_3)(N_3)]_2$ (**1**), $[Mn(L_2)(\mu_{1,1}\text{-}N_3)(N_3)]_2$ (**3**), $[Mn(L_3)(\mu_{1,1}\text{-}N_3)(N_3)]_2[(N_3)Mn(L_3)(\mu_{1,1}\text{-}N_3)(N_3)]_2$ (**4**) and $[Mn(L_4)(\mu_{1,1}\text{-}N_3)(N_3)]_2[Mn(L_4)(\mu_{1,1}\text{-}N_3)(N_3)]_2$ (**5**) and one new dicynamide bridged binuclear Mn(II) complex $\{[Mn_2(L_1)_2(dca)_2(H_2O)_2(\mu_{1,5}\text{-}dca)](ClO_4)\}$ (**2**) have been synthesized using the pyrimidine derived primary Schiff base ligands L_n ($n = 1$–4), with azide and dicynamide as bridging ligands. All the five complexes were characterized by elemental analyses, IR spectroscopy and single crystal X-ray crystallography, together with magnetic measurements of **1**–**4**. The tridentate Schiff base ligands are the [1 + 1] condensation products of 2-hydrazino-4,6-dimethyl pyrimidine with 2-acetyl pyridine, pyridine-2-carbaldehyde, 2-benzoyl pyridine and di(2-pyridyl) ketone for L_n ($n = 1$–4), respectively. All the complexes except **2** contain Mn(II)-azido links in which the Mn(II) centres are bridged by a di-$\mu_{1,1}$-azido (double EO) group. The double EO bridging fragments in the complexes are similar with bridging angles (Mn–N–Mn) ranging from 102.59° to 104.81°. Magnetic property studies reveal that in **1**, **3** and **4** intramolecular ferromagnetic interactions are mediated through the EO azido bridges with J parameters in the range 4.3–5.12 cm^{-1}, while a weak antiferromagnetic interaction prevails in **2** ($J = -0.12$ cm^{-1}) *via* $\mu_{1,5}$-dicynamide bridges. In addition, complexes **1**, **3** and **4** show weak intermolecular antiferromagnetic interactions ($J = -0.025$ to -0.027 cm^{-1}).

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1. Introduction

The construction of transition-metal supramolecular arrays based on covalent or hydrogen bonding interactions are an area of great research activity in inorganic chemistry. From a magnetic point of view, covalent systems are particularly interesting as they can provide high magnetic ordering. A rational design of these arrays implies that the selection and employment of appropriate bridging ligands which can mediate magnetic coupling between local spin carriers has allowed us to access a variety of high nuclearity products with interesting structural and magnetic properties. Our strategy is to use potential bridging ligands, such as azide [1] or dicyanamide [2,3], having versatile binding modes and conformational flexibility in the synthesis of new Mn(II) complexes [4,5]. The coordination modes of the azide ligand greatly affect the nature and magnitude of the magnetic exchange interactions in dinuclear complexes. Magnetic coupling mediated through an azide bridge is normally ferromagnetic [6,7] for the end-on mode (1-1,1 or EO) and antiferromagnetic for the end-to-end mode (1-1,3 or EE) [8,9]. On the other hand, the appropriate choice of metal ions along with the bridging ligands is also an important factor for such works. Among the first-row transition metal ions, high-spin Mn(II) centers are quite desirable because they contain the highest possible number of unpaired electrons [10]. To date, the reported Mn(II)-azido coordination compounds include one-dimensional (1D) chain complexes [11], two-dimensional (2D) layer complexes [12,13], three-dimensional (3D) framework complexes [14,15] and polynuclear complexes [16,17]. Dicyanamide (dca) has been shown to be a versatile ligand which may coordinate to metal ions as a terminal ligand through the nitrile nitrogen [2,18] or amide nitrogen [2,18], a μ_2-1,3-bridge through the amide nitrogen and one nitrile nitrogen [2,18], and an end-to-end μ_2-1,5 bridge through two nitrile nitrogen atoms with weak antiferromagnetic coupling [2,18], and also a μ_3-1,3,5 bridge through all of the nitrogen atoms, showing weak or strong ferromagnetic coupling [2,18]. As a matter of fact, dca can be utilized as a useful connector between metal centers to form higher-dimensional molecular frameworks having interesting structures and molecular properties. In continuation, using

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manganese(II) perchlorate as the metal precursor, four new azide bridged dinuclear manganese(II) complexes, $[Mn(L_1)(\mu_{1,1}\text{-}N_3)(N_3)]_2$ (**1**), $[Mn(L_2)(\mu_{1,1}\text{-}N_3)(N_3)]_2$ (**3**) $[Mn(L_3)(\mu_{1,1}\text{-}N_3)(N_3)]_2[Mn(L_3)(\mu_{1,1}\text{-}N_3)(N_3)]_2$ (**4**) and $[Mn(L_4)(\mu_{1,1}\text{-}N_3)(N_3)]_2[Mn(L_4)(\mu_{1,1}\text{-}N_3)(N_3)]_2$ (**5**), and one new dca bridged binuclear manganese(II) complex, $\{[Mn_2(L_1)_2(dca)_2(H_2O)_2(\mu_{1,5}\text{-}dca)](ClO_4)\}$ (**2**), have been synthesized (Scheme 1). We report here the synthetic details, spectral characterizations and X-ray crystal structures of **1**, **2**, **3**, **4** and **5**, and the magnetic properties of **1**–**4**, where the pseudohalides (azide, dca) act as terminal ligands as well as bridges ($\mu_{1,1}$; $\mu_{1,5}$) in the presence of the primary ligands.

2. Experimental

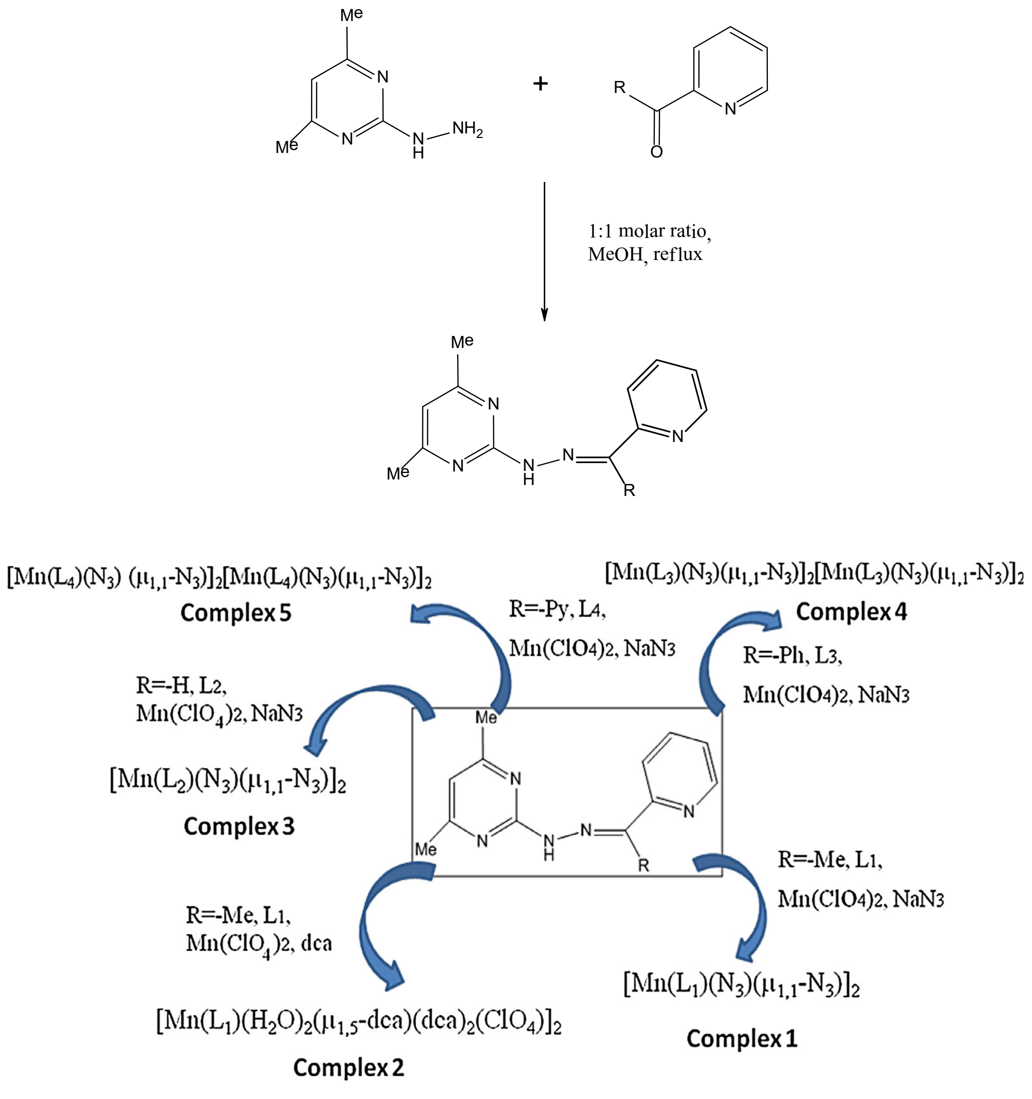
2.1. Materials

All chemicals were of reagent grade, purchased from commercial sources and used without further purification. Pyridine-2-carbaldehyde, 2-acetyl pyridine, 2-benzoyl pyridine and di(2-pyridyl) ketone were purchased from Aldrich. The other commercially available chemicals and solvents were used and purified by standard procedures.

Caution! Although we have not encountered any problems, it should be kept in mind that perchlorate compounds of metal ions are potentially explosive in the presence of organic ligands. Only a small amount of the material should be prepared and it should be handled with care.

2.2. Physical measurements

The infrared spectra of the complexes were recorded on a Perkin–Elmer RX I FT-IR spectrophotometer with KBr discs (4000–400 cm^{-1}). Elemental analyses (C, H and N) were carried out using a Perkin–Emer 2400 II elemental analyzer.^1H NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer using trimethylsilane as an internal standard in d_6-DMSO for ligands L_3 and L_4. The electronic spectra of **1**, **2**, **3**, **4** and **5** in purified methanol solution were recorded on a Hitachi model U-3501 spectrophotometer. The magnetic studies of **1**–**4** were carried out on polycrystalline samples using a Quantum Design MPMS-XL SQUID magnetometer operating in the 300–2 K temperature range and 0.05–0.7 T. Pascal's constants were utilized to estimate the diamagnetic corrections, the value in each case being subtracted from the experimental susceptibility data to give the molar magnetic susceptibility (øM).



Scheme 1. Schematic representation of the ligands (L_1, L_2, L_3 and L_4) and their complexes (**1**–**5**).

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