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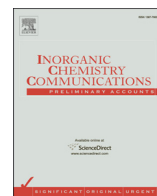
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Short Communication

Magnetic and spectroscopic properties of a 2D Mn(II) coordination polymer with carbohydrazone ligand



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ABSTRACT

A new 2D coordination polymer of Mn(II), $\{[\text{Mn}_2(\text{L})(\mu\text{-dca})_3]\cdot\text{CH}_3\text{OH}\}_n$ (**1**), has been synthesized and characterized by elemental, TGA and single-crystal X-ray diffraction analyses and spectroscopic methods where HL is bis-[(*E*)-*N'*-(phenyl(pyridin-2-yl)methylene)]carbohydrazone. Single crystals X-ray analysis reveals that **1** has dinuclear enolate bridged Mn(II) cores which are connected together by three $\mu_{1,5}$ -dicyanamide ($\mu\text{-dca}$) bridging ligands and a 2D coordination polymer is formed by these connections. FT-IR spectroscopy and X-ray analysis indicate that the carbohydrazone ligand is coordinated to the metal cores as a mononegative ligand in the enol form. The FT-IR spectrum of **1** depicts three characteristic bands of dicyanamide anion at 2179, 2239 and 2304 cm^{-1} . The magnetic susceptibility measurement of **1** between 2 and 295 K indicates the antiferromagnetic coupling mediated via enolate oxygen within the dinuclear cores, whereas the dicyanamide ligand connecting these dinuclear units does not provide any appreciable contribution to magnetic properties.

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Due to the peculiar structure diversity of coordination polymers and their potential application as functional materials in various fields, the design and synthesis of novel coordination polymers is still one of the interesting research fields in inorganic and synthetic coordination chemistry [1]. On the other hand, there is continuous interest in the chemistry of manganese complexes due to their biological relevance and exciting magnetic properties. Manganese complexes have been used as model systems for metalloenzymes [2], and are unique target molecules for mimicking several biological systems like the active centre of oxygen-evolving complex (OEC) in Photosystem II [3] and Mn-containing superoxide dismutase [4]. Manganese complexes may possess large number of unpaired electrons, making them appealing precursors for magnetic materials and consider as attractive materials for studying on magnetic exchange interactions [5]. The reaction of metal ions with the mixture of organic ligands and suitable bridging groups is one of the most successful methods for the design of coordination polymers [6]. The pseudohalide anions ($\text{N}(\text{CN})_2^-$, N_3^- , SCN^- , etc.) are one of the attracting group of bridging ligands which also play an important role in the magnetic exchange pathways between paramagnetic metal ions [7]. Among the bridging pseudohalide ions, dicyanamide anion has higher tendency to form coordination polymers which can

be attributed to the large size of this ligand and its several coordination modes [8,9].

Carbohydrazone based ligands obtained by the reaction of carbohydrazone with 2-pyridylketones in 1:2 M ratio are symmetric multidentate ligands in hydrazone family (Scheme S1) which are ideal precursors for designing transition metal complexes. This type of ligands has high tendency to coordinate into two metal ions through dicompartmental N_2O -donor groups which the oxygen atom usually acts as bridging atom between two metal ions [10]. Although carbohydrazone ligands could form interesting coordination compounds with unpredictable properties, there are only few reports on their complexes. The limited studies on this kind of ligands show direct reaction of carbohydrazone ligands with transition metal ions like Fe [11], Zn [12], Co [13] and Cu [14] generates $[2 \times 2]$ tetranuclear grid complexes. However, mononuclear [15] and dinuclear [16] complexes of carbohydrazone ligands are also known. Using the mixture of carbohydrazone ligands together with an appropriate bridging group like pseudohalides is one of the efficient methods for obtaining coordination polymers with a high chance. Nevertheless, the studies in this area are abnormally rare and limited only to the use of azide group [17]. Taking the advantages of the coordination ability of carbohydrazone ligands, recently we reported crystal structure and magnetic properties of a tetranuclear Mn(II) complex [17c] and Cr_2Na_2 [17d] complex with azide bridges. By considering the ability of dicyanamide bridging group in forming coordination polymers [18], in

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the present work we report synthesis, characterization, crystal structure and magnetic behavior of a 2D coordination polymer of Mn(II) with carbohydrazone and dicyanamide ligand.

The ligand bis-[(*E*)-*N'*-(phenyl(pyridin-2-yl)methylene)]carbohydrazone (HL) was synthesized and characterized according to our previous report [17c]. The reaction of HL, manganese(II) chloride tetrahydrate and sodium dicyanamide in 1:2:4 M ratios leads to a 2D coordination polymer of Mn(II), $[\text{Mn}_2(\text{L})(\mu\text{-dca})_3\cdot\text{CH}_3\text{OH}]_n$ (**1**) as orange crystalline material. Experimental part together with the details of synthesis is given in electronic supplementary information (ESI) file. The FT-IR spectrum of **1** depicts three characteristic bands of dicyanamide anion at 2179, 2239 and 2304 cm^{-1} which were attributed to the $\nu_{\text{sym}}(\text{CN})$, $\nu_{\text{asym}}(\text{CN})$ and $\nu_{\text{sym}} + \nu_{\text{asym}}(\text{CN})$ modes, respectively [19]. By comparing FT-IR spectrum of **1** with free ligand it is seen the C=O band of ligand was eliminated in the IR spectrum of **1** (Fig. S1). This finding suggests enolization of the amide functionality upon coordination to the metal ions in **1**. The absence of $\nu(\text{C}=\text{O})$ and appearance of a new band at 1614 cm^{-1} , which may be assigned to the $-\text{C}=\text{N}-\text{N}=\text{C}-$ moiety [20], also confirms this finding. The broad band at about 3200 cm^{-1} in the IR spectrum of **1** is due to the presence of N—H bond and confirms the presence of an amidic hydrogen atom. Disappearance of the carbonyl stretching vibration band, $\nu(\text{C}=\text{O})$, and the presence of N—H band suggests the absence of delocalization in the $(-\text{N}=\text{C}-\text{O})^-$ group in the coordinated ligand $(\text{L})^-$ [21]. The very broad band around 3400 cm^{-1} in the IR spectrum of **1** is attributed to the O—H groups of the uncoordinated methanol molecules involving hydrogen bonding interactions. UV-Vis spectrum of HL (Fig. S2) shows three bands at 214, 296 and 384 nm which are attributed to $\pi \rightarrow \pi^*$ (214, 296 nm) and $n \rightarrow \pi^*$ (384 nm) transitions. The UV-Vis spectrum of compound **1** shows a broad absorbance band at 385 nm which is due to the charge transfer (LMCT) transitions. The bands at 211 and 263 nm are due to intraligand transitions.

The crystal structure of **1** was determined by X-ray crystallography and the crystallographic information are given in Table S1 (see ESI file). The molecular structure and labeling of the atoms for the compound **1** are displayed in Fig. 1 and selected bond lengths and angles are collected in Table S2. Diffraction studies reveal that two-dimensional coordination polymer is built up of $[\text{Mn}_2(\text{L})(\mu\text{-dca})_3]$ units. The carbohydrazone ligand is coordinated to the Mn(II) ions as a pentadentate mononegative ligand, $(\text{L})^-$. The asymmetric part of **1** contains an enolato bridged dinuclear unit of Mn(II) which is converted to a 2D coordination polymer by three dicyanamide bridging groups. In compound **1**, both Mn(II) cores have distorted octahedral coordination environments (Fig. S3) as $\text{mer}[\text{Mn}(\text{L}^{\text{N}2-\mu\text{-O}})(\mu\text{-dca})_3]$ with oxygen and two nitrogen atoms provided by the Schiff base ligand in which the oxygen atom of carbohydrazone ligand, O11, share a position of adjacent Mn(II) ions. The Mn1—O11—Mn2 angle is $126.58(11)^\circ$ and Mn1...Mn2 distance through this line is $3.949(2)\text{ \AA}$. Two Mn1 and two Mn2 ions are connected together by two dca bridging ligands in which the Mn1...Mn1ⁱⁱ ($ii = 1 - x, 2 - y, 1 - z$) distance is $7.533(4)\text{ \AA}$ and Mn2...Mn2ⁱⁱⁱ ($iii = 2 - x, 1 - y, 1 - z$) distance equals to $7.580(4)\text{ \AA}$. The Mn1 and Mn2 ions also are connected together by third dicyanamide bridging group with the Mn2...Mn1^{iv} distance of $8.715(4)\text{ \AA}$ ($iv = -1 + x, y, z$). The equatorial plane of two Mn(II) ions is built from carbohydrazone donor atoms together with a dca bridging ligand. Fig. 2 shows two-dimensional polymeric sheets of **1**.

In **1** the Mn—O and Mn—N bond lengths are close to other reported Mn(II) complexes with N₂O-donor hydrazone based ligands [22]. The C72—N32 and C72—N22 bond lengths are $1.379(5)$ and $1.345(4)\text{ \AA}$, respectively. Comparison of these bond lengths indicates that the C72—N22 bond length (in which its hydrogen atom has been eliminated during complexation) is shorter than the C72—N32 bond length (hydrogen atom has been eliminated on the N32 atom after complexation).

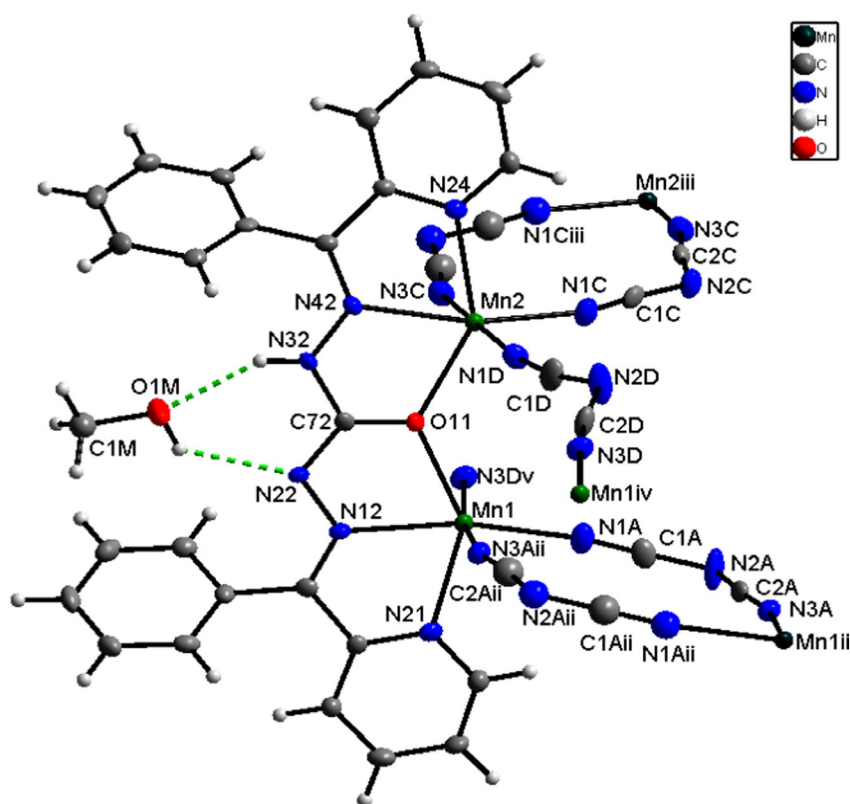


Fig. 1. DIAMOND plot of the part of polymeric structure of $[\text{Mn}_2(\mu\text{-L})(\mu\text{-dca})_3]_n$ (**1**) with thermal ellipsoids drawn at the 50% probability level. Disordered part of dca was omitted for clarity. Symmetry codes: $ii = 1 - x, 2 - y, 1 - z$; $iii = 2 - x, 1 - y, 1 - z$; $iv = 1 + x, y, z$; $v = -1 + x, y, z$.

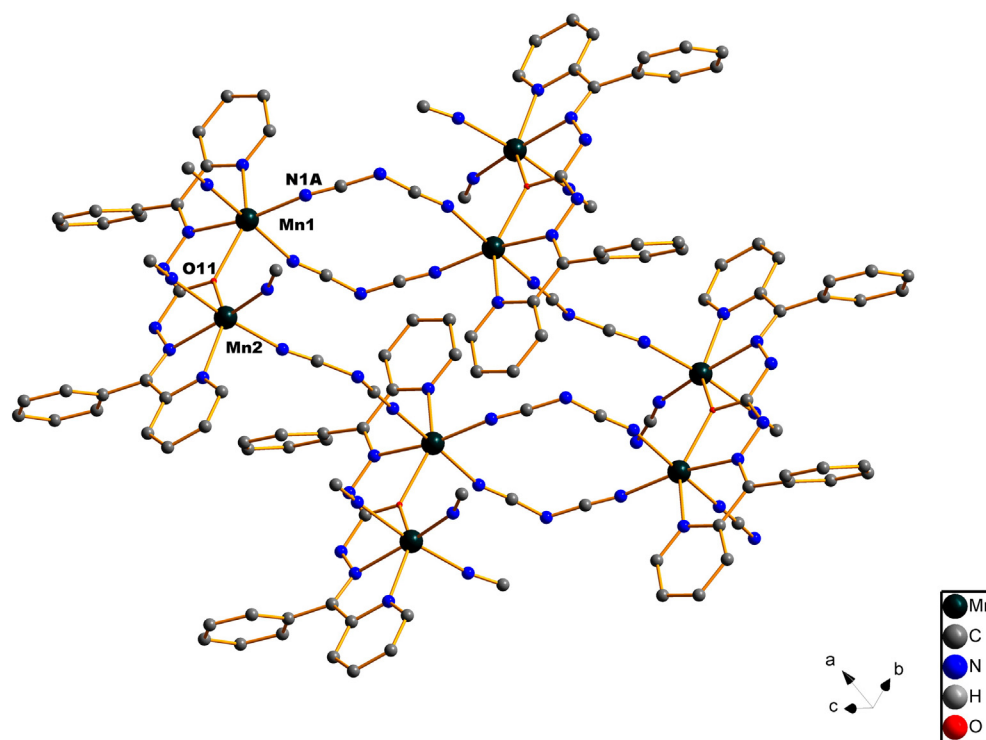


Fig. 2. Two dimensional polymeric sheets of compound **1**.

In addition, the length of C72—O11 bond is 1.283(4) Å in **1**, and is close to the bond length of C—O groups in the reported complexes containing the enol form of *N*-arylidene hydrazone ligands [23]. Moreover, this bond length is considerable longer than the C=O bond length in free cabohydrazone based ligands which is 1.217(3) Å [24]. All of these findings express the enolization through N22—C72—O11 and as a result the carbohydrazone ligand acts as mononegative ligand in **1**. Uncoordinated methanol solvent molecules are connected to carbohydrazone ligand by O—H...N and N—H...O hydrogen bonds (Fig. 1, Table S3).

To examine thermal stabilities of **1**, thermogravimetric analysis (TGA) was made in the static atmosphere of nitrogen. TGA curve of **1** (Fig. S4) shows that the uncoordinated methanol molecules remove in the range of 60–300 °C [starting mass 6.250 mg, observed 0.315 mg (5.04%), calcd. 0.263 mg (4.21%)]. This curve indicates that **1** is stable up to 370 °C, where the dca ligands are removed in the range of 370–600 °C [observed 1.67 mg (26.72%), calcd. 1.63 mg, (26.07%)]. Finally carbohydrazone ligand is removed during two steps to form the final product which is estimated to be Mn₂O₃.

Magnetic properties of **1** were determined by means of the magnetic susceptibility measurements performed at an applied magnetic field of 0.5 T between 2 and 295 K (Fig. 3). Analysis of the magnetic measurement was performed with the julX program (E. Bill, Max-Planck Institute for Chemical Energy Conversion, Mülheim/Ruhr, Germany) based on the spin Hamiltonian formalism [25]. Full-matrix diagonalization of the spin Hamiltonian for exchange coupling and Zeeman splitting was done with the routine ZHEEV from the LAPACK numerical package. Parameter optimization was performed with the simplex routine AMOEBA from NUMERICAL RECIPES. The room temperature $\chi_M T$ values of 8.41 cm³ mol⁻¹ K for **1** is close to the expected spin only values for two Mn(II) high-spin ions (8.75 cm³ mol⁻¹ K) with $S = 5/2$. On lowering the temperature the magnetic moments of **1** tend to zero at 2 K, indicating overall antiferromagnetic coupling. The more detailed analysis was done based on structural information. From the structural point of view **1** consists of dinuclear enolato bridged {Mn₂L} units which are connected by dicyanamide into 2D polymeric structure. However, the

μ -1,5-dicyanamide bridge is known as a very poor mediator for magnetic exchange, and practically non-coupled systems are observed in the literature [26]. From this reason the magnetic data of **1** were analyzed according to the simple dimer model, Eq. (1).

$$H = -2JS_1 \cdot S_2 + g\mu_B(\vec{S}_1 + \vec{S}_2) \vec{B} \quad (1)$$

Temperature-independent paramagnetism (TIP) and a Curie-behaved paramagnetic impurity (PI) with spin $S = 5/2$ were included according to $\chi_{\text{calc}} = (1 - PI) \cdot \chi + PI \cdot \chi_{\text{mono}} + TIP$. Best fit parameters are $g = 2.00$, $J = -1.7 \text{ cm}^{-1}$, $PI = 2\%$ and $TIP = 6.4 \cdot 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$. The coupling constant via enolic oxygen in **1** (-1.7 cm^{-1}) is very similar to previously reported values of -1.3 cm^{-1} for tetranuclear Mn(II) cluster, as could be expected from

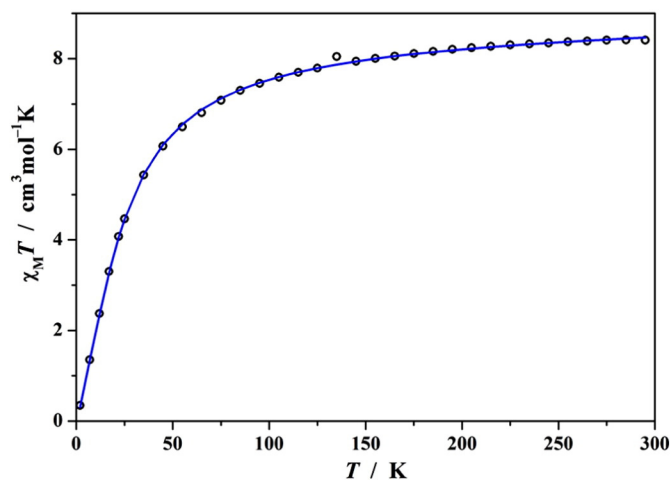


Fig. 3. $\chi_M T$ vs. T plot for **1** at an applied magnetic field of 0.5 T. Solid line represents the calculated curve fit (see text).

the almost identical Mn—O—Mn bond angles (126.74° for **1** and 126.42° for Mn(II) cluster) [17c].

Conclusions

In summary, a new 2D coordination polymer of Mn(II) has been prepared by the reaction of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ with carbohydrazone ligand and $\text{NaN}(\text{CN})_2$ in methanol. This compound was characterized by spectroscopic methods (FT-IR, UV–Vis), TGA analysis and single crystal X-ray analysis. The repetitive unit of 2D polymeric network in **1** incorporates a dinuclear Mn(II) unit which connected together by enolate oxygen atom and converts to 2D polymeric network by three dicyanamide bridging groups. Enolate bridged unit mediates moderate antiferromagnetic interaction, but there is not considerable magnetic interaction via dicyanamide bridges.

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Appendix A. Supplementary material

CCDC 1055096 contains the supplementary crystallographic data for **1**, which can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>. Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.inoche.2016.06.014>.

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