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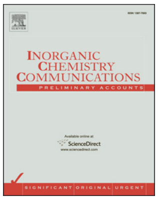

Short communication

Synthesis, structure and magnetic properties of a tetranuclear Mn(II) complex with carbohydrazone based ligand

Rahman Bikas [a,*], Hassan Hosseini-Monfared [a], Milosz Siczek [b], Serhiy Demeshko [c], Behzad Soltani [d], Tadeusz Lis [b]

[a] Department of Chemistry, Faculty of Science, University of Zanjan, 45371-38791 Zanjan, Iran
[b] Faculty of Chemistry, University of Wroclaw, Joliot-Curie 14, Wroclaw 50-383, Poland
[c] Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany
[d] Department of Chemistry, Faculty of Science, Azarbaijan Shahid Madani University, 53714-161 Tabriz, Iran

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ABSTRACT

A new tetranuclear complex of Mn(II), $[Mn_4(L)_2(CH_3OH)_2(\mu\text{-}N_3)_4(N_3)_2]\cdot 2(CH_3OH)$ (**1**), was synthesized and characterized by spectroscopic methods, single-crystal X-ray diffraction analysis and TGA analysis where HL is bis-[(*E*)-*N*′-(phenyl(pyridin-2-yl)methylene)]carbohydrazide. Single crystal X-ray analysis reveals that **1** has a Mn_4 core in which Mn(II) ions are connected by azide and enolate oxygen atoms. IR spectroscopy and X-ray analysis indicate that the carbohydrazone is coordinated to the metal cores as a mononegative ligand in the enol form. The magnetic behavior of **1** was investigated between 2 and 295 K and indicated that the magnetic coupling mediated via azide bridge is ferromagnetic whereas the enolate oxygen mediates antiferromagnetic coupling that leads to overall antiferromagnetic behavior.

The chemistry of multinuclear transition metal complexes is nowadays a broad and interdisciplinary research field in coordination chemistry. These compounds can be used as unique target molecules for mimicking the biological systems [1], and are attractive materials to study magnetic exchange interactions when they have paramagnetic metal ions in their structures [2]. In the area of magnetism, these compounds are appealing candidates for a building block to design new magnetic materials like single-molecule magnets (SMMs) [3]. Controlled preparation of multinuclear complexes with pre-established structures, properties and functions is one of the challenges in synthetic coordination chemistry [4]. The reaction of metal ions with a mixture of organic ligands and suitable bridging groups like azide is one of the most successful methods for the design of polynuclear transition metal complexes [5].

Carbohydrazide based ligands are special type of symmetric multidentate ligands in hydrazone family (Scheme 1) which are ideal precursors to design tetranuclear complexes [6]. Recently, tetranuclear lanthanide complexes of carbohydrazone and azide mix-ligands have been reported as polymetallic compounds with SMM behavior [7]. Metal complexes with mixed ligands of carbohydrazone Schiff bases and azide are rare although combination of different properties of these bridging groups and carbohydrazone ligands could form interesting compounds [8]. Taking the advantages of the coordination ability of azide bridging ligand and carbohydrazones in forming multinuclear metal complexes [8,9], herein we report the synthesis, characterization, crystal structure and magnetic behavior of a tetranuclear coordination complex of Mn(II).

All chemicals and solvents were purchased from Acros and used as received without further purification. IR spectra were recorded in KBr disks with a Bruker FT-IR spectrophotometer and UV–Vis spectra of solutions were recorded on a thermo spectronic, Helios Alpha spectrometer. Thermal gravimetric analysis (TGA) curve was recorded with a SETSYS Evolution TGA instrument. The temperature dependent magnetic susceptibility measurement was performed with a Quantum Design SQUID MPMS XL-5 magnetometer in the temperature range 295 to 2 K at the applied magnetic field of 0.5 T. Compound **1** was synthesized by the reaction of HL, $MnCl_2\cdot 4H_2O$ and sodium azide using the thermal gradient method in methanol as solvent (see ESI file).

The reaction of carbohydrazide with two equivalents of 2-benzoylpyridine led to pentadentate Schiff base ligand, HL, in high yield and purity (see ESI file). The expected keto-enol tautomeric structures of HL are illustrated in Scheme 1. It was found that HL is stable in keto form. In the IR spectrum of HL, two bands at 3361 and 3323 cm^{-1} (due to N–H) and very strong band at 1689 cm^{-1} (due to C=O stretching vibration) confirm the existence of free HL in keto form [10]. The reaction of HL, manganese(II) chloride tetrahydrate and sodium azide in 1:2:4 M ratios in methanol leads to a tetranuclear Mn(II) complex, $[Mn_4(L)_2(CH_3OH)_2(\mu\text{-}N_3)_4(N_3)_2]\cdot 2(CH_3OH)$ (**1**). In the IR

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[*] Corresponding author.
E-mail address: bikas_r@yahoo.com (R. Bikas).

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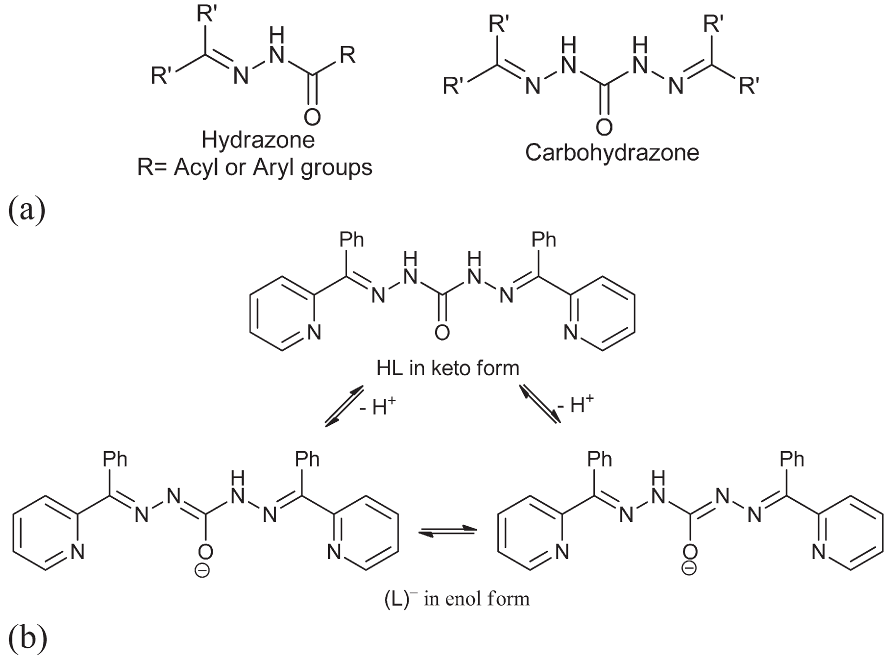

Scheme 1. (a) Hydrazones general formula and carbohydrazone; (b) tautomeric form of the HL.

spectrum of **1** a very strong band appears at 2067 cm^{-1} which attributed to the azide stretch and coordination of N_3^- to the manganese ion [11]. By comparing IR spectrum of complex **1** with that of free ligand (Fig. S1), it is seen that the C═O band is absent in the complex. This finding suggests enolization of the amide functionality upon coordination to the metal ions in **1**. The absence of ν(C═O) and appearance of a new band at 1614 cm^{-1}, which can be assigned to the –C═N–N═C– moiety [12] also confirm this finding. The broad band at 3188 cm^{-1} in the IR spectrum of complexes is due to presence of N–H bond and confirms the presence of amidic hydrogen. Disappearance of the carbonyl stretching vibration band, ν(C═O), and the presence of N–H band suggest the absence of delocalization in the –N–C═O group in the coordinated ligand $(L)^-$[13]. UV–Vis spectrum of HL (Fig. S2) shows three bands at 214, 296 and 384 nm, based on their extinction coefficients they can be attributed to $\pi \rightarrow \pi^*$ (214, 296 nm) and $n \rightarrow \pi^*$ (384 nm) transitions. The UV–Vis spectrum of compound **1** in methanol (Fig. S2) shows two broad absorbance bands at 518 and 395 nm due to the charge transfer (LMCT) transitions [14]. The band at 218 nm and shoulder at about 259 nm are intraligand transitions.

The molecular structure of **1** was determined by single crystal X-ray crystallography (see Table S1). The molecular structure and labeling of the atoms for compound **1** are displayed in Fig. 1 and selected bond lengths and angles are given in Table S2. Diffraction studies of **1** reveal a centrosymmetric structure. The carbohydrazone ligand is coordinated to the Mn(II) ions as a pentadentate mononegative ligand, $(L)^-$. The asymmetric part of the unit cell in **1** contains an enolato bridged dinuclear moiety of Mn(II) which is transformed to tetranuclear complex by an inversion symmetry operation ($i = -x + 1, -y + 1, -z + 1$). In compound **1**, both Mn(II) cores have distorted octahedral coordination environment (Fig. S3) with three nitrogen atoms from azides, oxygen and two nitrogen atoms provided by the Schiff base ligand. Oxygen atom of carbohydrazone ligand, O1, bridges adjacent Mn(II) ions. The Mn1–O1–Mn2 angle is 126.42(5)° and Mn1···Mn2 distances through this line is 3.998(2) Å. Two azide bridging ligands connect Mn1 ion to another $Mn2^i$ ion in end-on fashion. Therefore, the Mn1 ion is connected to two Mn2 ions via two different bridging groups, EO-azides and enolic oxygen atoms. The bridging azide groups span the axial positions of one metal center and the basal position of the other and the Mn_2N_2 cyclic unit is approximately planar. In this four membered cyclic unit the $Mn1\cdots Mn2^i$ distance is 3.370(1) Å. The equatorial positions of the two independent Mn(II) ions are the same and the only difference in the coordination environment between the two metal centers consists in one of the axial positions, which is a terminal monodentate azide for Mn1 but a methanol molecule for Mn2. The O–H···N hydrogen bonds join the axial ligands to each other and have considerable effect on distortion from ideal octahedral arrangement. In this compound, the intramolecular $Mn1\cdots Mn1^i$ and $Mn2\cdots Mn2^i$ distances are 5.256(2) and 5.202(2) Å, respectively. The Mn–O and Mn–N bond lengths are close to other reported Mn(II) complexes with N_2O-donor hydrazone based ligands [15]. The C1–N1 and C1–N3 bond lengths are 1.3782(18) and 1.3323(18) Å in **1**. Comparison of these bond lengths indicates that the C–N bond length (in which its hydrogen atom has been eliminated on complexation) is shorter than C–N bond length in which hydrogen atom remains on the nitrogen atom. In addition, the length of C1–O1 bond is 1.2742(16) Å in **1** which is considerably longer than the C–O bond length in free carbohydrazone based ligands (1.217(3) Å [16]). All of these findings express the enolization through N3–C1–O1. There are some weak C–H···N, C–H···O and π-stacking interactions between neighboring molecules stabilizing the crystal packing of **1** (Fig. S4, Table S2). Uncoordinated methanol solvent molecules are present in the crystal packing of **1** which are connected to carbohydrazone ligand by O–H···N and N–H···O hydrogen bonds (Fig. 1, Table S3). The red crystals of **1** become powder when they are removed from the mother liquor, which is attributed to the loss of the uncoordinated methanol molecules. Since the finger print IR spectra of the crystals and the corresponding powder are the same, we concluded that the complex is stable in spite of its change to powder form on drying. All spectroscopic and magnetic data also confirm the stability of the complex even in the powder form.

To examine thermal stabilities of **1**, thermogravimetric analysis (TGA) was made in the static atmosphere of nitrogen. TGA curve of **1** (Fig. S6) shows that the uncoordinated methanol molecules are removed between 40–100 °C [starting mass 13.658 mg, observed 0.752 mg (5.5%), calcd. 0.609 mg (4.45%)]. This curve also indicates that **1** is stable up to 125 °C, where the coordinated CH_3OH molecule is removed [observed 0.613 mg (4.49%), calcd. 0.609 mg (4.45%)] between 130–175 °C, then at 230 °C the N_3^- ligands are removed [observed 2.399 mg (17.56%), calcd. 2.397 mg, (17.52%)]. Finally

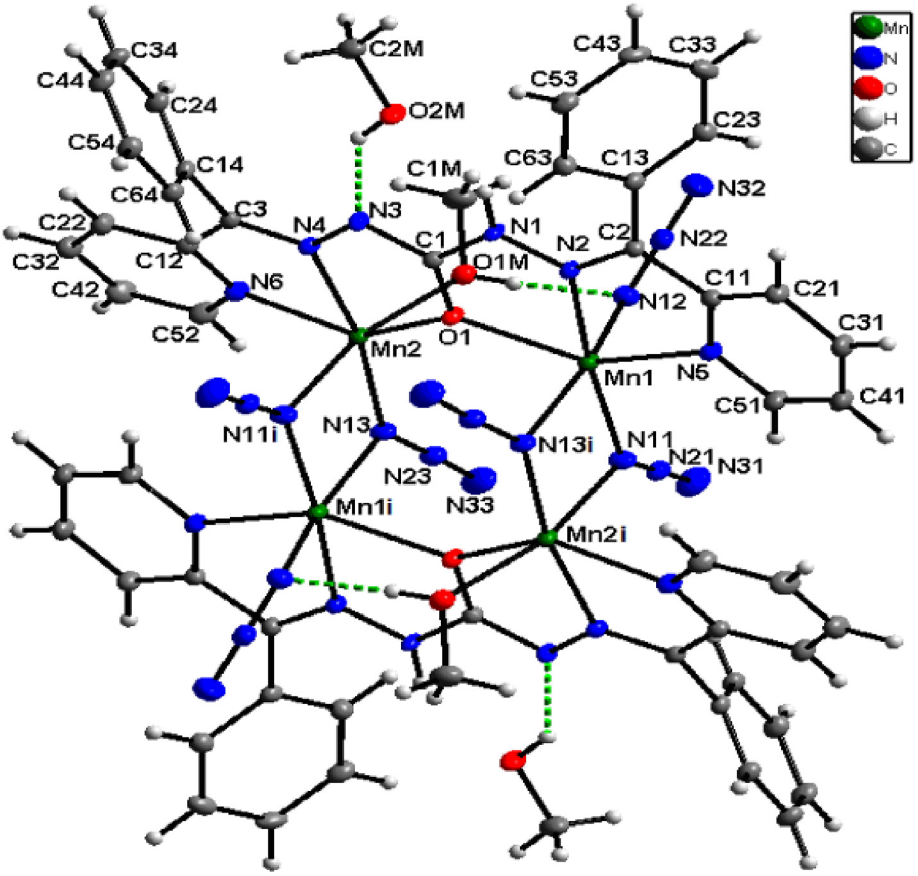

Fig. 1. DIAMOND plot of the molecular structure of $[Mn_4(L)_2(CH_3OH)_2(\mu\text{-}N_3)_4(N_3)_2]\cdot 2(CH_3OH)$ (**1**) with ADP ellipsoids drawn at the 50% probability level. Symmetry code: $i = -x + 1, -y + 1, -z + 1$.

aroylhydrazone ligand is removed during two steps at 330 and 410 °C. The overall mass loss up to 1000 °C is equal to $\Delta m \approx -9.704$ mg (-71.53%) of starting mass and indicates that the final product is MnO_2 (calcd. -75.84%).

Magnetic properties of **1** were determined by means of the magnetic susceptibility measurements performed at an applied magnetic field of 0.5 T between 295 and 2 K (Fig. 2). The room temperature $\chi_M T$ values of 16.8 $cm^3\ mol^{-1}$ K for **1** is close to the expected spin only values for four Mn(II) high-spin ions (17.5 $cm^3\ mol^{-1}$ K for $g = 2.0$) 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. According to the molecular structure of **1**, four existing interaction pathways can be divided into two groups, one mediated by the $(\mu\text{-}1,1\text{-}N_3)_2$ linkage and one by enolic oxygen. The appropriate Heisenberg–Dirac–van-Vleck (HDvV) spin Hamiltonian includes two isotropic exchange coupling constants (J_1 and J_2) and Zeeman splitting, where g is the Lande factor, $\hat{S}$ is the spin angular momentum and μ_B is the Bohr magneton, Eq. (1).

$$H = -2J_1\left(\hat{S}_1\hat{S}_2 + \hat{S}_3\hat{S}_4\right) - 2J\left(\hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3\right) + \sum_{i-1}^{4} g\mu_B\, \vec{B}\,.\vec{S}_i. \tag{1}$$

Temperature-independent paramagnetism (*TIP*) was included according to $\chi_{calc} = \chi + TIP$[17]. Best fit parameters are $g = 1.98$, $J_1 = +1.1\ cm^{-1}$, $J_2 = -1.3\ cm^{-1}$ and $TIP = 1.8 \times 10^{-4}\ cm^3\ mol^{-1}$. The Hamiltonian in Eq. (1) is symmetric, therefore assignment of J_1 and J_2 to the concrete pathways is not known a priori, but requires consideration of magneto-structural correlations. Some $(\mu\text{-}1,1\text{-}N_3)_2$ bridged dimanganese(II) complexes show moderate ferromagnetic coupling with J values ranging from $+0.8\ cm^{-1}$ to $+2.6\ cm^{-1}$[18,19]. Theoretical calculation also predict ferromagnetic coupling in Mn-$(\mu\text{-}1,1\text{-}N_3)_2$-Mn complexes for the bridging Mn–N–Mn angle $\alpha > 100°$ [20]. According to this correlation, the positive coupling constant $J_1 = +1.1\ cm^{-1}$ can be unambiguously attributed to the $(\mu\text{-}1,1\text{-}N_3)_2$ linkage ($\alpha_{av.} = 100.85°$), therefore the negative coupling constant $J_2 = -1.3\ cm^{-1}$ describes the exchange interaction via enolic oxygen.

Additionally to the curve shape of $\chi_M T$ versus T plot, the energy level calculation (see Fig. S7) also confirms the $S_T = 0$ ground state for **1**. The first exited state $S_T = 1$ lies only 1.4 cm^{-1} above the ground state, followed by a quasi-continuous spectrum of spin multiplets up to $S_T \le 10$.

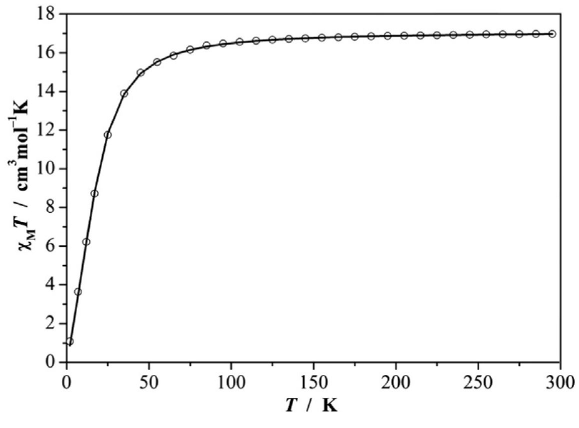

Fig. 2. $\chi_M T$ vs. T plot at an applied magnetic field of 0.5 T for **1**. Solid line is the best fit to the model described in Eq. (1) (see text).

In summary, a new tetranuclear complex of Mn(II) was prepared by the reaction of $MnCl_2 \cdot 4H_2O$ with carbohydrazone ligand and NaN_3 in methanol. This complex was characterized by spectroscopic methods (IF, UV–Vis), TGA and single crystal X-ray analyses. The tetranuclear core in **1** incorporates two different bridged units mediating ferro- and antiferromagnetic interactions, the combination of them gives rise to an overall $S_T = 0$ ground state. Magnetic couplings were rationalized based of the common magnetostructural correlations for end-on azido and enolato linkages.

Acknowledgments

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Appendix A. Supplementary data

CCDC 1055097 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.2015.10.021.

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