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H-bonded supramolecular synthon induced magnetic superexchange phenomenon results weak ferromagnetic and strong antiferromagnetic interactions in two new copper-orotate coordination network

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ABSTRACT

Hydrothermal self-assembly of orotic acid ($C_5H_4N_2O_4$=OrH_3) with metal salt $Cu(Ac)_2{\cdot}H_2O$ yielded a new OrH based hydrogen bonded coordination network of formula $[Cu(OrH)(2NH_3)(H_2O)]{\cdot}H_2O$ (**1**) and $[Cu(OrH)(2NH_3)]_2$ (**2**). Single crystal X–ray study on **1** confirms that +2 charges on the metal ions (Cu^{2+}) are balanced by OrH anion. N–H···O and O–H···O hydrogen bonding synthons are the only artifact for the resulting hydrogen bonded copper-OrH architecture. Temperature dependent measurements of magnetic susceptibility reveals the occurrence of competitive exchange interactions with a net ferromagnetic character in **1** (J = +0.48 cm^{-1}) and strong antiferromagnetic interaction in **2** (J = −4.93 cm^{-1}). Magnetic superexchange interaction transmitted through equatorial–axial hydrogen bridge system promotes weak ferromagnetic interactions in **1** while in **2** it is in basal-basal position, in which two d_{x2-y2}orbitals is involved in exchange mechanism reveals the coexistence of two antiferromagnetic exchange pathways, intramolecular much stronger than intermolecular. The natural bond orbital (NBO) analysis applied separately to α and β spin density matrices clearly shows two important magnetic superexchange pathway with shorter Cu···Cu contact 5.542(4) Å and 4.845(4) Å or 5.755(1) Å in (**1**) and inter dimer 6.665(1) Å and 4.6744(9) Å for (**2**).

1. Introduction

Coordination complexes, assembled by non-covalent directional forces involving hydrogen bonded supramolecular synthons as potential connecter, are sometimes adopt different crystal packing due to changes occur in their molecular structures [1]. The hydrogen bonded metal-organic network shows intriguing architecture and potential application in various areas including different exchange coupling patterns, offering exciting possibilities in the designing of single molecular magnets (SMM) and/or single chain magnets [2].

In molecular magnetism [3a,3b] whereas magnetic exchange couplings between metal ions are realized usually through coordination bonds, the possibility of observing magnetic exchange through weak supramolecular interactions such as hydrogen bridges has been reported for complexes based on diverse metal centers such as V(IV) [3c], Cr(III) [3d], Fe(II) [3e], Fe(III) [3f], Co(II) [3g,3h], Ni(II) [3i,3j], and mixed-metal binuclear complexes[3k]. Moreover, numerous examples of H-bonded dinuclear Cu(II) complexes have also been already described experimentally and addressed theoretically [3l,3m,4].

From magneto-structural point of view copper chemistry is a very extensively studied area, both experimentally and theoretically, especially with respect to hydrogen bonded binuclear systems [3l,3m,4]. These Cu(II) complexes exhibit ferromagnetic or antiferromagnetic coupling depending on their geometry and are also of theoretical interest, because they provide examples of the simplest case of magnetic interactions with only one unpaired electron. Achieving ferromagnetic and antiferromagnetic coupling between the metal ions having noncovalent contacts (>4.0 Å) is a challenging task. In this regard, the N-containing heterocyclic ligands are studied most frequently not only due to their strong coordination ability of nitrogen atoms with most transition metal ions by coordination bonds, but also due to their rigid skeleton structures and abundant recognition sites for further assembling

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into higher-dimensional multifunctional supramolecular frameworks through non-covalent interaction like hydrogen bonding, π···π stacking and Van der Waals' forces [5].

In this context, Orotic acid (OrH_3, vitamin B13) have been used as the coupler between metal ions in the present study, because of its multidentate functionality and also it occupies a singular position among the free pyrimidines, being the only precursor for pyrimidine bases of nucleic acids in living organisms [6]. Since in OrH ion, the carboxylate anion and carbonyl group is a versatile H–bond acceptor while imino group is an H–bond donor, these peripheral groups are expected to interact with each other or with ancillary ligands via hydrogen bonding, of pyrimidyl ring [Scheme ESI 1].

Herein we have reported a new OrH based hydrogen coordination network of formula $[Cu(OrH)(2NH_3)(H_2O)]\cdot H_2O$ (**1**), and re-synthesized **[**$Cu(OrH)(2NH_3)]_2$ (**2**) [6e]. Although both the complexes were synthesized hydrothermally at same temperature (120 °C) in presence of 25% ammonia solution but the formation of complexes (**1** and **2**) depends on the duration of reaction time. The longer (72 h) hydrothermal condition leads to formation of **2** with the loss of the lattice and coordinated water molecules as compared to **1** (24 h) [Scheme ESI 2] that has a key effect on regulating the molecular geometry and magnetic interaction. In $[Cu(OrH)(2NH_3)(H_2O)]\cdot H_2O$ (**1**) (**1**), Cu(II) is in distorted square planar geometry forming hydrogen bonded Cu (II) dimer that leads to exhibit a net, very weak ferromagnetic interactions whereas in $[Cu(OrH)(2NH_3)]_2$ (**2**), the metal ion is in distorted square pyramidal geometry with monomeric figure shows strong antiferromagnetic coupling.

To the best of our knowledge, the temperature dependent measurements of magnetic susceptibility that reveals the occurrence of competitive exchange interactions with a net ferromagnetic character was observed for first time in **1** among all reported metal-OrH complexes till date [5h,6]. The magnitude of this exchange coupling has been conveniently described in **1** as a sum of ferro- (J_F) and antiferromagnetic (J_{AF}) terms according to Kahn"s model. Susceptibility measurements on this compound indicate a ferromagnetic, albeit weak, coupling between the two paramagnetic centers, with best-fit values of $J = +0.48\ cm^{-1}$, $\theta = +5.45$ K and $g_{av} = 2.14$. Complex **2** exhibits much stronger antiferromagnetic properties ($J = -4.93\ cm^{-1}$, $\theta = -6.45$ K, and $g_{av} = 2.109$) which is a result of the coexistence of two antiferromagnetic exchange pathways, intramolecular much stronger than intermolecular. The inspection of the crystal packing of **2** allows us to suggest, that superexchange interaction through {···O–Cu–N–H} contact should be the strongest interaction, the Cu···Cu distance is the shortest one (4.244(2)Å), the angles (158.94(2)°) are closets to the optimal values. A quantitative investigation has been performed by means of *ab* initio density functional theory based calculations in the broken-symmetry approach for both the complexes.

2. Experimental

2.1. Material and method

All chemicals of reagent grade were commercially available and were used without further purification. Orotic Acid, $Cu(Ac)_2\cdot H_2O$, were purchased from Sigma Aldrich and used as such.

2.1.1. Synthesis of $[Cu(OrH)(2NH_3)(H_2O)]\cdot H_2O$ (1)

0.5 mmol Orotic Acid, 0.5 mmol $Cu(Ac)_2\cdot H_2O$, 0.5 mmol Zn $(Ac)_2\cdot 2H_2O$ and 5 ml 25% ammonia solution was taken in a 7 ml Teflon reaction vessel. The reaction vessel was then placed in a stainless steel reactor and heated at 120 °C in a high precision programmed oven at the heating rate of 20 °C/h for a period of 24 h. After heating the reaction vessel was cooled at the same rate as it was heated. The blue clear solution thus obtained was filter and kept for crystallization at room temperature. After five days air stable blue block shaped crystals suitable for X-ray diffraction were collected.

2.1.2. Synthesis of $[Cu(OrH)(2NH_3)]_2$ (2)

The title compound was re-synthesized by different method to as done earlier by I. Mutikainen et al. [6e] and having same crystal structure which is not discussed.

77 mg (0.25 mmol) Orotic Acid, 60 mg (0.25 mmol) $Cu(NO_3)_2.3H_2O$, 110 mg (0.25 mmol) $Dy(NO_3)_3.5H_2O$ and 5 ml 25% ammonia solution was taken in a 7 ml Teflon reaction vessel. The reaction vessel was then placed in a stainless steel reactor and heated at 120 °C in a high precision programmable oven at the heating rate of 20 °C/h for a period of 72 h. After heating the reaction vessel was cooled at the same rate as it was heated. The blue clear solution thus obtained was filter and kept for crystallization at room temperature. After two days air stable blue block shaped crystals suitable for X-ray diffraction were collected.

2.2. Analysis and physical measurements

Magnetic measurements in the temperature range 1.8–300 K were performed using a Quantum Design SQUID-based MPMSXL-5-type magnetometer. The SQUID magnetometer was calibrated with the palladium rod sample (Materials Research Corporation, measured purity 99.9985%). The superconducting magnet was generally operated at a field strength ranging from 0 to 5 T. Measurements were made at a magnetic field of 0.5 T. Corrections were based on subtracting the sample – holder signal and contribution χ_D estimated from the Pascal constants [7]. A temperature–independent paramagnetism of $60 \times 10^{-6}\ cm^3\ mol^{-1}$ K for copper (II) ion in $[Cu(OrH)(2NH_3)(H_2O)]\cdot H_2O$ (**1**) was used for calculations. Magnetization measurements were conducted at 2 K in the magnetic field from 0 to 5 T.

2.3. Crystal structure determinations

Single crystal of **1** with a dimension 0.30 × 0.20 × 0.10 respectively were mounted on Bruker Apex DUO CCD area-detector (fine-focus sealed tube equipped radiation source) with a graphite monochromator and Mo Kα radiation (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 100(2) K.

The structure was solved by the direct methods, and refined by the full-matrix least-squares based on F^2 with anisotropic displacement parameters for the non-hydrogen atoms using x-Area (data collection, cell refinement and data reduction) SHELXS-97 (structure solution), and SHELXL-97 (structure refinement) and Bruker SHELXTL (molecular graphics) [8]. An empirical method was used for adsorption correction for **1**. Hydrogen atoms were included in geometrically calculated positions using a riding model. Lattice parameters and refinement for **1** is given in Table 1.

2.4. DFT calculations

DFT approach [9] (B3LYP)[9a,9b] with the basis sets LanL2DZ (D95V(d,p) basis set for all non-metal atoms [9c] combined with the LanL2DZ for Cu, as implemented in the GAUSSIAN'09 software package [9d], was used to optimize geometry without any symmetry restrictions and wave number calculations were carried out to verify whether the optimized molecular structure corresponded to minimum energy. DFT functional are not able to describe long range London dispersion interaction, we corrected the (semi) local density functional with the original D3 damping