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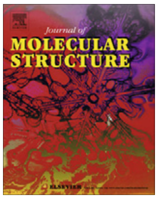

π–π Stacking and magnetic coupling mechanism on a mono-nuclear Mn(II) complex

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ABSTRACT

A novel magnetic coupling is observed in a unpublished crystal that consists of a mono-nuclear manganese(II) complex, namely, $[Mn(DPP)(NCS)_2]$ (DPP = 2-(3,5-dimethyl-1H-pyrazol-1-yl)-1,10-phenanthroline), in which neutral DPP molecule functions as tridentate chelated ligand. In the complex Mn(II) ion assumes a distorted trigonal bipyramidal geometry and in the crystal there is a π–π stacking interaction between the adjacent complexes, which involves pyridyl ring and the symmetry-related pyrazolyl ring and pyridyl ring. The fitting for the data of the variable-temperature magnetic susceptibilities with infinite uniform Mn(II) chain formula gave the magnetic coupling constant $J = -0.11\ \mathrm{cm}^{-1}$, and theoretical calculations reveal that there exists a very weak anti-ferromagnetic coupling between the adjacent Mn(II) ions with $J = -0.02\ \mathrm{cm}^{-1}$. The magnetic coupling sign is explained based on McConnell I spin-polarization mechanism with the analysis of the spin density population and the factors that dominate the magnetic coupling magnitude.

1. Introduction

For a long time, the field of molecular magnetism has attracted considerable attention, and major advances have been made in both their description and their application as new molecular-based materials [1–3]. In the magnetostructure research, it is very important to obtain the basic information about magnetic coupling magnitudes and associated mechanism. In order to obtain this information many fitting models or fitting formulas have been developed and practiced, for example, on binuclear system [4], trinuclear system [5–8], tetranuclear system [9–15] and one-dimensional system [16–21]. At the same time, theoretical calculations also have been successfully developed and practiced to reveal the factors that may dominate the magnetic coupling in binuclear system [22–31] and trinuclear system [32,33]. Mostly, fittings and calculations deal with the systems where the coupling metallic ions are connected by bridging ligands, namely, the magnetic interactions are through bond exchange. In the materials science area, the π–π stacking interaction as one of the intermolecular forces has been playing a pivotal role. For example, the π–π stacking interaction resulted in a silver complex displaying a highly electrical conducting behaviour [34], and it also led to a change in the fluorescent emission intensity for some compounds [35]. In the magnetic coupling area, π–π stacking interaction also plays an important role. For example, some authors attributed the strong ferromagnetic order to π–π stacking interaction [36], and other authors found the π–π stacking interaction led to a strong anti-ferromagnetic interaction between spin-carriers [37–39]. In a word, the π–π stacking interaction should be one of the key factors that dominant magnetic coupling, and it may be used to design ideal molecule-based magnets. But the papers on fitting treatment and theoretical calculations of the magnetic coupling of π–π stacking systems are very scarce and mostly, these papers only deal with radicals or complexes with radicals as ligands to our knowledge [37–42]. And in the area only the magnetic coupling signs of a few compounds have been explained with McConnell I spin-polarization mechanism and McConnell II charge transfer mechanism [43,44], and the factors that dominate the magnetic coupling mechanism have not been mentioned by them. Therefore, it is interesting and meaningful work to design and synthesize complexes with π–π stacking and to study the factors that dominate magnetic coupling signs and coupling magnitude.

2-(3,5-Dimethyl-1H-pyrazol-1-yl)-1,10-phenanthroline is one of ideal ligands that possess both strong chelated coordination group and larger conjugation plane which may be used to form complexes with strong π–π stacking and relevant magnetic coupling pathway, but up to now no such complexes have been reported except for three mono-nuclear Cd(II) complexes to our

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knowledge [45–47]. The interest in magnetic coupling mechanism of π–π stacking system resulted in us synthesizing the title mononuclear complex, and here we report its synthesis, crystal structure and magnetic coupling mechanism involving both experimental fitting and theoretical calculations.

2. Experimental

2.1. Materials

2-(3,5-Dimethyl-1H-pyrazol-1-yl)-1,10-phenanthroline was synthesized through the reaction of 2-chlorine-1,10-phenanthroline and 3,5-dimethyl-1H-pyrazole and all other chemicals are analytical grade and used without further purification.

2.2. Preparation of [Mn(DPP)(NCS)$_2$]

Methanol solution (5 ml) of NaSCN (0.0131 g, 1.62×10^{-4} mol) was added into 20 ml methanol solution containing $Mn(ClO_4)_2 \cdot 6H_2O$ (0.0583 g, 1.61×10^{-4} mol) and 2-(3,5-dimethyl-1H-pyrazol-1-yl)-1,10-phenanthroline (0.0434 g, 1.58×10^{-4} mol), and the mixed solution was stirred for a few minutes. The yellow single crystals were obtained after the filtrate was allowed to stand slow evaporation at room temperature for about 2 weeks. IR (cm^{-1}): 2053(s), 1608(m), 1583(m), 1563(m), 1512(s), 1364(s), 846(s). Elemental anal. Calcd. for $C_{19}H_{14}MnN_6S_2$: (fw 445.42) C, 51.23; H, 3.17; N, 18.87; Mn, 12.33. Found: C, 51.45; H, 3.44; N, 18.41; Mn, 12.89%.

2.3. Physical measurements

Infrared spectra were recorded with a Bruker Tensor 27 infrared spectrometer in the 4000–500 cm^{-1} region using KBr disks. C, H and N elemental analyses were carried out on a Perkin–Elmer 240 instrument and the Mn element content analysis was performed on an atomic absorption spectrophotometer, Model Z-8000. Variable-temperature magnetic susceptibilities of microcrystalline powder sample were measured in a magnetic field 1 K Oe in the temperature range 2–300 K on a SQUID magnetometer. The data were corrected for the magnetization of the sample holder and for the diamagnetic contributions of the complex which were estimated from Pascal's constants.

2.4. Computational details

The magnetic interaction between Mn(II) ions were studied on the basis of density functional theory (DFT) coupling with the broken-symmetry approach (*BS*) [48–50]. The exchange coupling constants *J* have been evaluated by calculating the energy difference between the high-spin state (E_{HS}) and the broken symmetry state (E_{BS}). Assume the spin Hamiltonian is defined as:

$$\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 \tag{1}$$

If the spin projected approach is used, the equation proposed by Noodleman [48–50] to extract the *J* value for a binuclear transition-metal complex is thus:

$$J = \frac{E_{BS} - E_{HS}}{4S_1S_2} \tag{2}$$

For all the models, where $S_1 = 5/2$, $S_2 = 5/2$ for Mn(II) ion, from Eq. (2), we get the expression:

$$J = \frac{(E_{BS} - E_{HS})}{25} \tag{3}$$

While with the non-projected approach proposed by Ruiz et al. [51]:

$$2J = \frac{E_{BS} - E_{HS}}{2S_1S_2 + S_2} \tag{4}$$

where S_1 and S_2 are the total spins of the two interacting paramagnetic centers and $S_1 > S_2$ is assumed for heterodinuclear complexes. For all the models, where $S_1 = 5/2$, $S_2 = 5/2$ for Mn(II) ion, from Eq. (4), we get the expression:

$$J = (E_{BS} - E_{HS})/30 \tag{5}$$

To obtain exchange coupling constants *J*, Orca 2.8.0 calculations [52] were performed with the popular spin-unrestricted hybrid functional B3LYP proposed by Becke [53,54] and Lee et al. [55], which can provide *J* values in agreement with the experimental data for transition metal complexes [56]. Tri-ζ with one polarization function def2-TZVP [57,58] basis set proposed by Ahlrichs and coworkers for all atoms was used in our calculations. Strong convergence criteria was used in order to ensure that the results are well converged with respect to technical parameters (the system energy was set to be small than 10^{-7} hartree).

2.5. X-ray crystallographic analysis of the complex

A yellow single crystal of dimensions 0.16 × 0.12 × 0.05 mm was selected and subsequently glued to the tip of a glass fiber. The determination of the crystal structure at 25 °C was carried out on an X-ray diffractometer (Bruker Smart-1000 CCD) using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Corrections for L_p factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and refined as riding. The programs for structure solution and refinement were SHELXS-97 and SHELXL-97, respectively. The pertinent crystallographic data and structural refinement parameters are summed in Table 1.

3. Results and discussion

3.1. Crystal structure of [Mn(DPP)(NCS)$_2$]

Fig. 1 shows the coordination diagram with the atom numbering scheme and Table 2 gives the coordination bond lengths and the associated angles. From Table 2 it can be known that the coordination bonds lengths range from 2.055(6) Å to 2.273(6) Å

Table 1
Crystal data and structure refinements for the complex.

Formula	$C_{19}H_{14}MnN_6S_2$
Mr	445.42
Crystal system	Monoclinic
Space group	$P2_1$
a(Å)	7.6271(18)
b(Å)	14.846(4)
c(Å)	8.668(2)
β(°)	102.927(4)
V(Å^3)	956.6(4)
Z	2
D_c (g cm^{-1})	1.546
μ (mm^{-1})	0.926
Reflections collected	5315
Unique reflections/R_{in}	3795/0.053
R_1 [$I > 2\sigma(I)$]	0.0744
wR_2 (all data)	0.1192
GOF	0.937
$\Delta\rho_{max}$ (e Å^{-3})	0.539
$\Delta\rho_{min}$ (e Å^{-3})	−0.277