Dalton Transactions

Accepted Manuscript

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Dalton Transactions

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Thermal and Light induced Spin Crossover Behavior of a Dinuclear Fe(II) Compound

Received 00th January 2015,
Accepted 00th January 2015

DOI: 10.1039/x0xx00000x

www.rsc.org/

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A dinuclear Fe(II) compound has been prepared through the reaction of 2,5-dichloride-4-phenylimino-1,2,4-triazole (L) with $Fe(BF_4)_2·6H_2O$, with the formula of $[Fe_2(L)_5(SCN)_4](H_2O)$ (1). X-ray, magnetic, and ^{57}Fe Mössbauer characterization showed that compound 1 exhibited spin crossover (SCO) behavior with $T_{1/2}$=150 K. The study figues out that introducing chloride groups on the ligand exerts a positive effect on increasing $T_{1/2}$ and making SCO more complete. LIESST effect was also observed for 1 through light irradiation experiment.

Spin Crossover (SCO), is a phenomenon that occurs in some metal complexes wherein the spin state of the complex changes due to external stimuli such as a variation of temperature, pressure, light irradiation or an influence of a magnetic field[1]. The 1,2,4-triazole system has been found to be particularly suited towards generating SCO behavior in Fe(II)-N_6 derivatives, among which the extensively studied system is 1D polymeric [Fe(4-R-1,2,4-triazole)$_3$](anion)$_2$ compounds (R=amino, alkyl, hydroxyalkyl)[1-4]. They perform outstanding spin crossover properties with high transition temperature near room temperature and large thermal hysteresis. The coordination chains of Fe(II) are connected by triple N1,N2-triazole bridges, the short, rigid linkage is what really makes the triazole 1D systems unique. But due to their polymeric structure, it is not easy to get single crystals, which brings difficulty to know their exact structure. Alternately, several dinuclear SCO compounds of Fe(II) , which are easier to get single crystals, are currently receiving great interest. These structures can keep the triple N1-N2-trizole bridges, which has main influence on the SCO properties. Dinuclear Fe(II) compounds, such as $[Fe_2(L1)_5(NCS)_4]·3.5MeOH$, L1=4-phenylimino-1,2,4-triazole[5] and $[Fe_2(L2)_5(NCS)_4]_3·4MeOH$ L2=N-salicylidene-4-amino-1,2,4-triazole[6], with Fe(II) ions linked by covalent bridging, could enhance the intra-cooperativity and efficiently transmit structural and electronic changes between the Fe(II) centers, and always using NCS^- as coligand to target perfect coordination field to give rise to SCO[7-9]. But as we know, the simple dinuclear compounds with triple bridges are very scarce [5, 6, 10-14]. Now we add a new family member to the dinuclear Fe(II) SCO systems and try to analyze the influence of properties of substituent on SCO behaviour. We tried to tune the SCO behavior by adding two chloride groups on the benzene ring of the ligand. The electron-withdrawing ability of chloride groups can adjust the ligand field and the distortion from ideal octahedral symmetry of the first coordination sphere. The comparison of the new dinuclear Fe(II) compound and the already known[5] member implies the

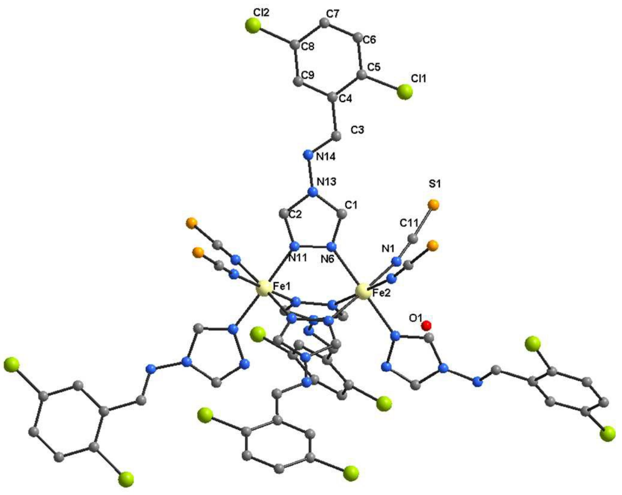

Fig.1 View of the molecular structure of **1** at 100 K.

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† Electronic Supplementary Information (ESI) available: crystal packing，magnetic properties graphs；X-ray crystallographic files for **1** in CIF format. CCDC 1059254 and 1059155. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x

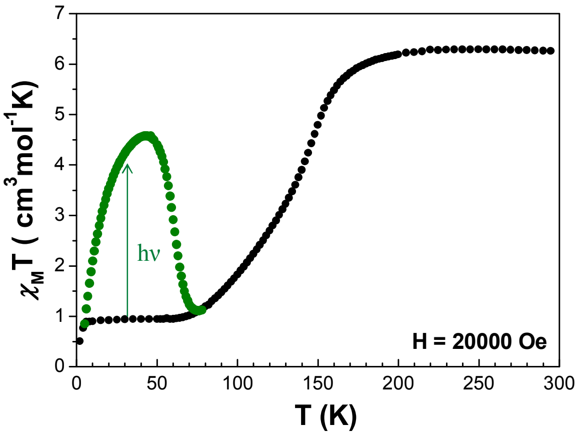

Fig. 2 LIESST effect of compound **1**, plot plots of $\chi_M T$ vs. T before (black) and after (green) light irradiation.

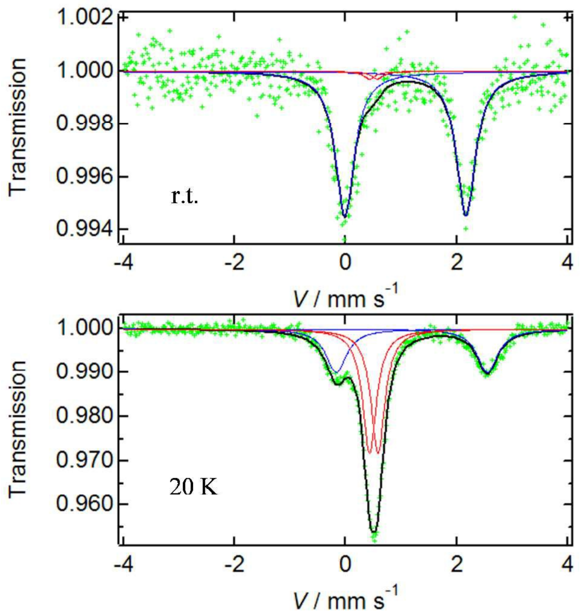

Fig.3 Mössbauer Spectroscopy of compound **1** of separate temperature.(Green dots: observed, black line: calculated, blue line: HS phase, red line: LS phase)

efficiency of introducing electron-withdrawing group would benefit for enhancing SCO behavior. LIESST effect could also be observed for the first time of all known compounds with similar structures [5, 6].

Crystal data and structural parameters of **1** are given in Tables S1 and S2 in the supplementary information. Crystal structure analysis of **1** at 100 K shows the triclinic space group $P\bar{1}$. The two Fe(II) centers are linked through three N1-N2-trizole bridges with the distance of 3.723(9) Å (Fig. 1). Each Fe(II) coordination sphere is completed further by three N atoms from one terminal triazole ligand and two cis-thiocyanate ligands. There are two chlorine substituents on the benzene ring of the ligand. The average Fe–N bond length at 100 K is 1.9792 Å. At 180 K, the $P\bar{1}$ space group is retained, but the Fe–Fe distance is stretched to 3.905(3) Å. The Fe–N bond length increases to 2.1485 Å. Meanwhile the colour of the crystal changes from deep red at 100 K to pale yellow at 180 K. Elongation of bond length and thermochromic effect clearly indicate possible process of SCO.

The temperature dependence of $\chi_m T$ (χ_m is the molar paramagnetic susceptibility) of compound **1** is derived from magnetization measurements in an applied field of 5 kOe and the temperature range 2–300 K (Fig.S2). At room temperature, the $\chi_m T$ value is 7.02 $cm^3 \cdot K \cdot mol^{-1}$, indicating that all Fe(II) ions are present in the HS state, as expected from the molecular structure analysis. As the temperature decreases, the sample shows an abrupt drop in magnetization in the temperature range from 165 K to 70 K. The $\chi_m T$ value is 0.74 $cm^3 \cdot K \cdot mol^{-1}$, indicating an incomplete SCO. The transition temperature ($T_{1/2}$) is estimated to be 150 K. The decrease of $\chi_m T$ value observed below 50 K may be due to the weak antiferromagnetic coupling of the remaining HS Fe(II) ions. The transition curves for the cooling and heating directions are identical. No hysteresis is observed.

Through π-π interaction between phenylimino and phenyl and weak interaction of Cl···π, the dinuclear units form chains, then further connected into 3D structure. The solvent molecule fills in the crystal structure by O-H···S hydrogen bond (Fig.S1).The weak inter- and intra-molecule interactions lead to a relatively flat spin crossover curve (Fig.S2).

The irradiation test of compound **1** (Fig.2) indicates the occurrence of LIESST (light-induced excited spin-state trapping) effect. The sample was cooled to 5 K and irradiated with 532 nm green laser (P = 10 mW/cm^2) for 2 h. After reaching photo-excited magnetic saturation, the laser was switched off. The $\chi_m T$ value increased abruptly before reaching a plateau at 4.6 $cm^3 \cdot K \cdot mol^{-1}$. Under such treatment, two Fe(II) ions were converted from LS to HS* phase. Then $\chi_m T$ value decreased from 45 K to 60 K after heating slowly under a 20 kOe field, which was due to relaxation from HS* to LS. According to the first derivative of the $\chi_m T$ vs. T curves, $T_{(LIESST)}$ was 61 K. There is also antiferromagnetic coupling of two HS* Fe(II) ions with the exchange interaction parameter J of -1.44 cm^{-1}.

In order to understand the SCO process for compound **1**, the Mössbauer spectra were measured as shown in Fig.3 and Fig.S3. Mössbauer parameters, (δ: isomer shift, ΔEQ: quadruple splitting, Γ/2: half width at half maximum) and relative area fraction (A) of HS and LS are summarized in Table S3. At room temperature, the spectrum is consisted of a single quadruple-split doublet which represents two HS Fe(II) centers (δ = 1.077 $mm \cdot s^{-1}$, ΔEQ =2.18 $mm \cdot s^{-1}$) with A^{HS} = 96.9%, and a shoulder peak represents a very small part of LS Fe(II) (A^{lS} = 3.1%) (δ = 0.50 $mm \cdot s^{-1}$, ΔEQ =0.14 $mm \cdot s^{-1}$). As temperature goes down, the ratio of LS Fe(II) increases and HS decreases, the SCO was fully confirmed by Mössbauer spectroscopy on cooling, the presence of a single iron site indicates a SCO mechanism that proceeds in one step and the two Fe(II) centers both exhibit SCO. At 20 K, there is still a considerable percent of HS Fe(II) (A^{HS} = 34.1%), illustrating an uncompleted SCO behavior.

Table 1 Distortion degree of compounds 1

Compound	Octahedron Distortion (HS)	SCO behaviour	T(SCO)
1	0.043/0.034	Incomplete	150 K
$[Fe_2(L1)_5(NCS)_4]·3.5MeOH$ L1=4-phenylimino-1,2,4-triazole[5]	0.086/0.132	Incomplete	115 K

In order to investigate the correlation between SCO properties with the molecular structure, we calculated the distortion degree from O_h symmetry of compound **1** using the method of continuous shape measures (CSM) [16]. Interestingly, we found that besides electronic effect of substituents on the benzene ring of the ligand, there may be another crucial factor that could influence the SCO behavior of the compound. As listed in Table 1, when the distortion degree of two Fe(II)N6 fragments of **1** are both below 0.1, the compound performs a comparatively complete SCO, but for Fe(II)N6 fragments of $[Fe_2(L1)_5(NCS)_4]·3.5MeOH$, one distortion degree is below 0.1 and the other one is above 0.1, the compound performs very incomplete SCO. It indicates that the smaller the distortion degree, the more complete SCO behavior. At the same time, the $T_{1/2}$ of **1** is 35 K higher than that for $[Fe_2(L1)_5(NCS)_4]·3.5MeOH$. For Fe(II) compounds with spin crossover properties, the $Fe(II)^{LS}N6$ configuration has been found to favor almost regular O_h symmetry, spin state transition from HS to LS also corresponds to the formation of FeN6 octahedron. So if a HS phase has taken a regular O_h symmetry, as the temperature decreases, it will promote the formation of FeN6 octahedron of LS Fe(II) and make it more easy to translate from HS to LS state, thus the occurrence of spin crossover. We calculate the deviation degree of two Fe(II)N6 configuration at the temperature of HS phase, as mentioned above, if deviation degree $<$ 0.1 for a HS phase, there is reasonable deduction that the compound will perform spin crossover.

A DFT (density functional theory) calculation [17] was also used to obtain HOMO, LUMO energy and electron affinity of the two ligands: 2,5-dichloride-4-phenylimino-1,2,4-triazole and 4-phenylimino-1,2,4-triazole (table S4). The energy of the orbitals actively involved in σ and π interactions is varied as the substitutions changed on the benzene ring. The calculation results showed the electron affinity of 2,5-dichloride-4-phenylimino-1,2,4-triazole is higher than 4-phenylimino-1,2,4-triazole. As proposed in the literature [17], the presence of low-lying LUMO orbitals and the consequent high electron affinity of 2,5-dichloride-4-phenylimino-1,2,4-triazole enables phenylimino group to show enhanced π back acceptance characteristics compared to 4-phenylimino-1,2,4-triazole, thus the stronger ligand field. That is the reason of introducing electron-withdrawing group would benefit to enhance the SCO behavior**.**

Conclusions

A new compound $[Fe_2(L)_5(SCN)_4](H_2O)$, where L is 2,5-dichloride-4-phenylimino-1, 2, 4-triazole, has been synthesized and magnetically characterized. An incomplete SCO can be observed. It also exhibits LIESST effect after irradiation at low temperature. Through comparison with another SCO compound with similar structure, we found that the SCO property is influenced by the substituent on the benzene ring of the ligand. In addition, the compound which the deviation degree of two FeN6 configuration from O_h symmetry below 0.1 may perform more complete SCO behaviour and higher $T_{1/2}$. The complex also provides a platform for photo-magnetic research of dinuclear compounds.

Acknowledgements

This work was supported by the Natural Science Foundation of China (21290171, 21321001), the National Basic Research Program (2013CB933401).

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