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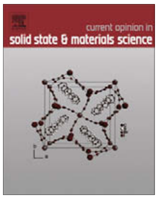

Design, structure, and properties of functional metal–ligand inorganic modules

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ABSTRACT

From the standpoint of supramolecular chemistry major advances have been made concerning the functional properties of metal–ligand-based coordination complexes/extended solids/polymers. This paper reviews recent results from our laboratories on two contemporary areas of research: (i) spin-crossover $Fe^{II}N_6$ complexes which are representative examples of molecular bistability and (ii) synthesis of tailor-made transition-metal-based 1D coordination polymers and investigation of their magnetic exchange phenomena from the standpoint of molecule-based magnetic materials. Our primary focus is on the magnetic properties which seem to hold promise for future applications. It has been shown that covalent bond-driven discrete complexes/coordination polymers are further stabilized by association due to multiple weak, noncovalent interactions. In the design of $Fe^{II}N_6$ complexes our laboratories have so far relied on synthesis of discrete molecules. However, they are connected by noncovalent interactions, imparting cooperativity.

1. Introduction

The directed assembly of coordination complexes into discrete entities or extended networks with predictable connectivity and dimensionality remains a particularly challenging task. The bottom-up construction of functional materials from molecules and ions is at the core of modern crystal engineering [1–13]. The construction of solid-state architectures and crystal engineering has become rapidly developing areas of research which have implications for the rational design of functional materials [9–13]. Much study has been centered upon the use of supramolecular contacts in particular hydrogen bonding – between suitable molecules to generate multi-dimensional arrays or networks. Although purely organic-based systems have become widely studied, their inorganic counterparts based upon metal–ligand coordination complexes are only recently receiving significant attention.

The discussion in this article is limited to two contemporary areas of research: (i) spin-crossover $Fe^{II}N_6$ complexes which are representative examples of molecular bistability and (ii) synthesis of tailor-made transition-metal-based coordination polymers and investigation of their magnetic exchange phenomena from the standpoint of molecule-based magnetic materials. Our primary focus is on the magnetic properties which seem to hold promise for future applications. This paper provides an overview of some of our recent results where noncovalent interactions have played a crucial role in bringing about drastic change in the spin-state behavior of $Fe^{II}N_6$ complexes. Understandably, every reference related to the topics of concern of this article cannot be cited and selection has had to be severely limited to major research groups working in these fields.

2. Spin-transition phenomena

The spin-crossover (SC) compounds are one of the representative examples of molecular bistability [12,14–23]. The SC phenomenon requires the crystal-field strength of the ligand to be of the same order of magnitude as the mean electron-pairing energy. The high-spin (HS) and low-spin (LS) states of an SC compound are interconvertible by several different physical perturbations such as temperature, pressure, light-irradiation as well as chemical modifications such as variation in the nature of associated counter-anion and the degree of solvation in the crystallized salts [18–20]. While SC behavior is essentially a phenomenon of a single molecule, the interaction between SC sites is an important factor to govern SC properties such as the abruptness of the spin-transition, hysteresis, and LIESST (light-induced excited spin-state trapping) effect (promotion of the ground LS state to a metastable HS state by irradiation at low temperatures), which are important properties for applications such as information storage, as optical switches in new electronic devices, molecular switches, and visual displays. In essence, for potential applications the spin-transition should be abrupt due to cooperative phenomena and occur with a thermal hysteresis which confers a memory effect on the system. Ideally, room-temperature should fall in the middle of the hysteresis loop. Thus the synthetic design of SC compounds exhibiting interactions between spin-transition sites is of current interest. Selected

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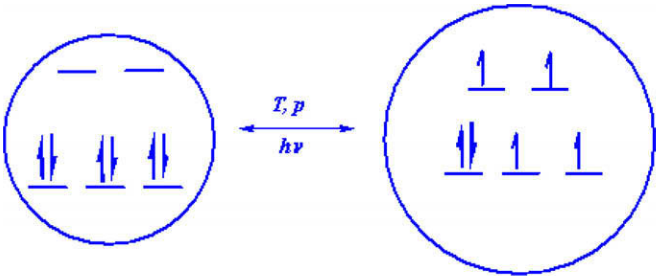

Fig. 1. Change in the spin-state of six-coordinate iron(II) as a function of external perturbations.

references of major contributors to this topic of research of relevance to our work are chosen from literature reports [24–34].

2.1. Fe^{II}N$_6$ complexes of nonplanar tridentate heterocyclic ligands

Six-coordinate iron(II) complexes, mostly those with an Fe^{II}N$_6$ coordination environment, may be diamagnetic [low-spin (LS; $S = 0$)], paramagnetic [high-spin (HS; $S = 2$)], or exhibit a HS $\rightleftharpoons$ LS transition that depends on the relative magnitude of crystal-field strength of the ligand and the mean electron-pairing energy. Two closely related aspects are to be taken into account to understand the SC mechanism: (i) how the spin-state change occurs at a molecular level and (ii) how this change spreads in the crystal lattice to result in the different kinds of spin conversions. It is generally accepted that SC phenomenon arises not only from the well-designed ligand with proper crystal-field strength but crystal packing interactions [through which various kinds of intra- and intermolecular cooperative interactions, including covalent-linkage among Fe^{II}N$_6$ coordination environments and noncovalent (hydrogen bonding, π–π stacking) and van der Waals interactions] also exert great influence on SC behaviour [16,21–23]. Thus, both spin conversion equilibrium ($T_{1/2}$) and cooperative aspects of the conversion (steepness of the conversion curve, hysteresis of first-order spin transition, if any) depend on subtle solid-state effects induced by noncoordinating counteranions, noncoordinating solvent molecules, or ligand substitution [21–23]. It is worth recalling that one-to-one correspondence between *effective* interactions specific to the model used to explain the observed behavior and *real* interactions present in the solid does not exist. At variance from magnetism, a pair of interacting SC units cannot be isolated without substantial changes in all properties, making the definition and measurement of a hypothetic SC interaction parameter by no means possible. It is admitted that all real interactions result in a long-range effective "elastic" interaction [35,36]. In other words, the cooperativity is mediated by the lattice, while short-range effective interactions could be correlated to the existence of covalent bonds [21–23].

Notably, the transition from HS ($^5T_2$) Fe^{II} to LS ($^1A_1$) Fe^{II} (Fig. 1) is associated with a change in magnetic moment, bond-length or complex size, and a thermochromic effect. The singlet-state is the thermodynamically more stable state. The sharpness of the effect and, in some cases, thermal hysteresis (see below) have been linked to strong intermolecular interactions (hydrogen-bonds, π–π interactions) or cooperative phenomena which triggers to spread the $\sim$10% (0.15–0.2 Å) Fe^{II}–ligand bond-length distortion over the entire crystal.

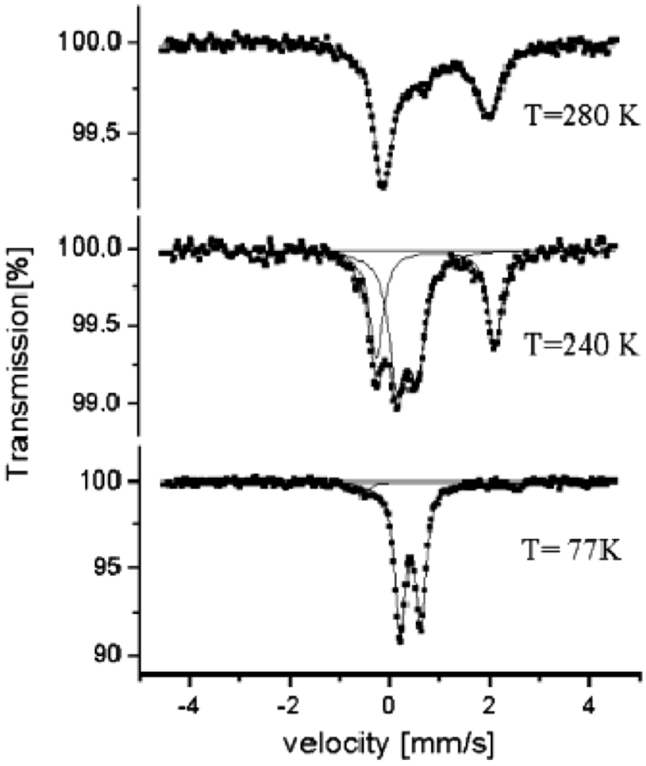

Fig. 3. ^{57}Fe Mössbauer spectra of $[Fe^{II}(L^1)_2][ClO_4]_2\cdot H_2O$ at three different temperatures (see Ref. [42]).

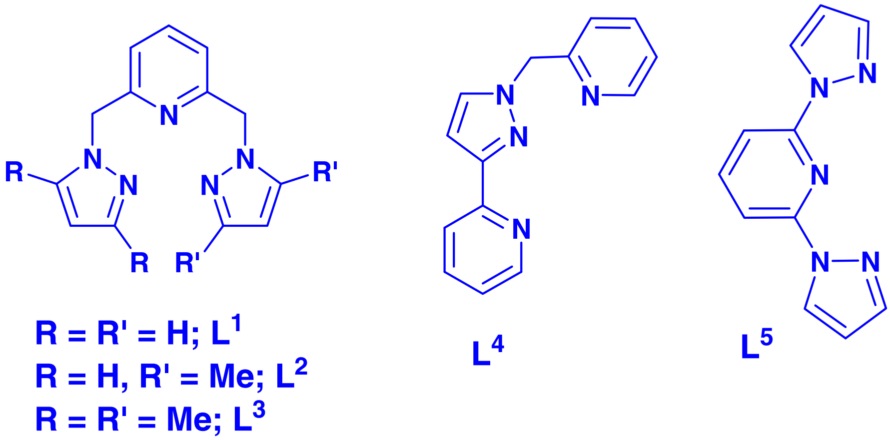

Fig. 2. The tridentate ligands of pertinence to this article.