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Coordination Chemistry Reviews 249 (2005) 2534–2548
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

Review

New trends of molecular magnetism

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Received 27 April 2005; accepted 20 May 2005
Available online 1 July 2005

Contents

Abstract

The history of molecular magnetism began in 1951 with the study of a dinuclear complex, copper(II) acetate [B. Bleaney, K.D. Bowers, Proc. R. Soc. A 214 (1952) 451], however it was not until the 1990s that it received a strong impetus with the discovery of the first molecular-based solids that exhibited spontaneous magnetization [R. Sessoli, D. Gatteschi, A. Caneschi, M.A. Novak, Nature 365 (1993) 141; D. Gatteschi, A. Caneschi, L. Pardi, R. Sessoli, Science 165 (1994) 1054]. Many important discoveries have been made since then by European teams in particular [ESF Scientific Programme Molecular Magnets (MM), October 2, 1999]: the synthesis of the first bimetallic molecular magnets and organic magnets with the highest Curie temperature known so far; the synthesis of room-temperature molecular-based magnets; the discovery of spin cross-overs that occur with large hysteresis at room temperature; new photomagnetic processes, including light-induced excited spin state trapping; the synthesis of the first molecular-based magnetic superconductor; the first characterization of the magnetic tunneling effect.

Keywords: Molecular materials; New ferromagnets; Ferrimagnets; Antiferromagnets

1. Introduction

Molecular materials are systems that may be considered as built of discrete molecules, the so-called “building blocks”. This structural feature creates great opportunities for the modeling of electrical, magnetic and optical properties of materials through the selection of appropriate constituent molecules. At the same time, it is also a challenge for developing new synthetic methods that would make it possible to control the directional arrangement of molecules in the space crystal lattice. In reality macro properties of materials

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doi:10.1016/j.ccr.2005.05.013

are always determined by the joint mutual interactions of molecules in the crystalline structure.

The faculty of Chemistry of University of Wrocław is not only the main polish center on coordination chemistry but also the place where investigation of molecular magnetism in Poland has started. It took place in the 1960s and in 1970s in the magnetic laboratory, equipped with a few modern susceptometers and magnetometers which were already functioning.

It is crucial that there is intense research cooperation with national and international scientific teams in many magnetic research areas.

We are approaching a period where we can expect a breakthrough in electronics as well as a transition from microelectronics to molecular electronics. We are heading towards the next stage of miniaturization of microelectronic elements and devices. This undoubtedly is one of the biggest challenges, which chemistry above all must rise to, by synthesizing new molecular materials with pre-programmed properties, with special attention to their molecular magnetic properties.

2. Molecular magnetism and new materials group (University of Wrocław, Wrocław)

2.1. Magnetism of dimeric copper(II) carboxylates

Copper(II) carboxylates have been extensively studied from different points of view because the carboxylato anions exhibit different bonding modes influencing their properties. Most of them are biologically active substances, metal-ion-drugs [5].

We have studied the magnetic properties of copper(II) in many compounds and the results were published in approximately 80 papers co-authored with Melnik and co-workers [6–8]. Examples include magnetic data for two dimeric complexes of general formulae: $[Cu\{L\}_2(X)]_2$ (**1**) (where L = 2-methylthionicotinate (2-MeSnic), and X = H_2O, CH_3OH, DMF, DMSO) and $[Cu\{2\text{-MeSnic}\}_2(py)_2]_2$ (**2**) (where py is pyridine) [6–8]. The magneto-structural characterization of these copper(II) complexes is important because of their biological activity.

The tetrakis(μ-carboxylato)-bridged Cu^{II} system (I) displays intramolecular antiferro-magnetic exchange coupling between two paramagnetic metal ions [9,10]. The strength of this coupling is measured by the coupling constant J within the usual isotropic Heisenberg–Dirac–van Vleck model: $H = -2JS_1S_2$; $S_1 = S_2 = 1/2$ ($2J$ represents the singlet–triplet energy gap). Very strong intramolecular antiferro-magnetic coupling has been observed in tetrakis μ-carboxylato-bridged Cu^{II} complexes ($2J \sim -300\,cm^{-1}$) depending on the nature of the carboxylic acid and the apical ligands [7,9,10, and references therein]. A dimeric Cu^{II} structure, in which very asymmetrically coupled Cu^{II} ions essentially do not interact, is rarely observed, complex (**2**) is in fact only the second example in the literature.

Fig. 2 (complex **1**) presents the χ_M versus T relationship, where χ_M is corrected molar magnetic susceptibility, and which shows a maximum at about room temperature, a feature characteristic of antiferromagnetically coupled copper(II) pairs. At low temperatures a contribution from a Cu^{II} mononuclear impurity can be observed.

The magnetic susceptibility data were best fitted to the modified Bleaney–Bowers equation [1]:

$$\chi_M^{corr} = \left\{ \frac{Ng_{dim}^2\beta^2}{3kT}\left[1 + \frac{1}{3}e^{-2J/kT}\right]^{-1}\right\}(1-x) + \left(\frac{Ng_{mom}^2\beta^2}{4kT}\right)x$$

where x is the percent of monomeric impurity and other symbols have their usual meaning. Minimization of the deviation $R = \sum(\chi_i^{calcd} - \chi_i^{expt})^2/(\chi_i^{calcd})^2$ was the criterion used to determine the best fit. Singlet–triplet energy gaps ($2J$) of all the complexes were found and compared.

The value of $|2J|$ for the copper(II) 2-methylthionicotinate dimers tends to increase according to the series of terminal ligands: DMSO < DMF < CH_3OH < H_2O.

Some workers have proposed that larger $2J$ values are attributed to a weaker σ-donation by the axial ligand, with suggestion that there is a corresponding increase in the ligand field of the four carboxylato oxygen atoms around the metal ion [9–11]. Our results maintain that the magnitude of magnetic coupling is rather sensitive to the Cu–O–C–O–Cu geometry, which depends more on steric effects of the terminal ligand than on its σ-donation (nucleophilicity) [7].

Another type of Cu^{II} dimer was obtained with 2-methylthionicotinic acid and pyridine ligands, (**2**) Fig. 1. The temperature dependence of the magnetic susceptibility and moment for $[Cu(2\text{-MeSnic})_2(py)_2]_2$ (**2**) is outlined in Fig. 2. The value of μ_{eff} 1.91 BM at 300 K decreases to 1.71 BM at 5 K and to 1.54 BM at 1.9 K. This behavior is consistent with very weak antiferromagnetic interaction between the copper(II) magnetic centers. The data were fit to the Bleaney–Bowers equation [1]. The best-fit parameters are: $2J = -1.30\,cm^{-1}$, $g = 2.12$, $R = 1.82 \times 10^{-3}$. The observed singlet–triplet energy gap of $-1.30\,cm^{-1}$ suggests that the magnetic orbitals are unfavourably oriented in this case to provide good overlap for a magnetic interaction [9]. The Cu···Cu separation 4.453 Å.

Psomas et al. [12] have described a novel dinuclear Cu^{II} complex of tetrakis[(2,4-dichlorophenoxy)acetato] bis(2,2′-bipyridylamine)dicopper(II) where two bridging carboxylate ligands are bound to two Cu^{II} metal ions in an asymmetric fashion with a Cu···Cu separation above 4.0 Å. The magnetic data show a very weak antiferromagnetic interaction between the two metal ions with $2J = -1.6\,cm^{-1}$. The complex $[Cu(2\text{-MeSnic})_2(py)_2]_2$ is only the second example of the abovementioned dinuclear structural type, in which the observed antiferromagnetic interaction is very weak [9].