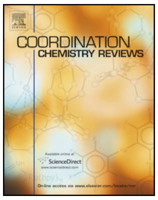
Coordination Chemistry Reviews xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Electron paramagnetic resonance of switchable copper-nitroxide-based molecular magnets: An indispensable tool for intriguing systems

Matvey V. Fedin[a,b,*], Sergey L. Veber[a,b], Elena G. Bagryanskaya[a,b,c], Victor I. Ovcharenko[a]

[a] International Tomography Center SB RAS, 630090 Novosibirsk, Russia
[b] Novosibirsk State University, 630090 Novosibirsk, Russia
[c] N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS, 630090 Novosibirsk, Russia

Contents

ARTICLE INFO

Article history:
Received 30 May 2014
Received in revised form 1 November 2014
Accepted 1 November 2014
Available online xxx

Keywords:
Molecular magnetism
EPR
Exchange interactions
Copper-nitroxide clusters
Spin crossover
Structural rearrangements

ABSTRACT

Copper-nitroxide-based molecular magnets of the $Cu(hfac)_2L^R$ family (often called “breathing crystals”) are interesting and appealing systems exhibiting various magnetic anomalies triggered by temperature or light, which can generally be viewed as spin-crossover-like phenomena. The presence of paramagnetic copper(II) ions and stable nitroxide radicals in the polymer chains of breathing crystals makes electron paramagnetic resonance (EPR) widely applicable to these systems. In addition to the determination of typical parameters (*g*-tensor, hyperfine splitting constants, etc.), EPR allows the monitoring of magnetostructural switching between different states and evaluation of exchange interactions in the exchange-coupled clusters of copper(II) with nitroxides and those between the exchange-coupled clusters. This review highlights the capabilities of EPR in investigating breathing crystals and demonstrates the obtaining of crucial information on magnetic interactions inaccessible by other techniques.

---

* Corresponding author at: ITC SB RAS, Institutskaya str. 3a, Novosibirsk 630090, Russia. Tel.: +7 383 3307547.
E-mail address: mfedin@tomo.nsc.ru (M.V. Fedin).

http://dx.doi.org/10.1016/j.ccr.2014.11.015
0010-8545/

1. Introduction

Switchable magneto-active compounds are being actively investigated in the field of molecular magnetism with the aim of creating building blocks for new types of ultra-dense magnetic memory, data processing, new types of sensors, etc. [1–5]. Among these, of particular interest are spin crossover (SCO) and related phenomena [2–5]. The ability of SCO compounds to change their magnetic properties in response to temperature variation, illumination with light, application of pressure, or other external stimuli underlies all of the above-mentioned potential applications. Therefore, SCO compounds were actively studied during the last decades by various physical methods, of which SQUID magnetometry, X-ray analysis, Mössbauer spectroscopy and UV/vis optical spectroscopy are probably the most important techniques. However, EPR was rarely used for SCO compounds, mostly because electron relaxation is very fast for typical high-spin ions (such as iron or cobalt) at temperatures of interest.

The "breathing crystals" Cu(hfac)$_2$L^R (where hfac is hexafluoroacetylacetonate, and L^R is a pyrazolyl-substituted nitroxide ligand) represent a new family of switchable molecular magnets based on copper(II) ions bridged by stable nitroxide radicals (Fig. 1) [6–14]. In many compounds crystals also include solvent molecules (Solv) located in the inter-chain space (Cu(hfac)$_2$L^R·0.5Solv).

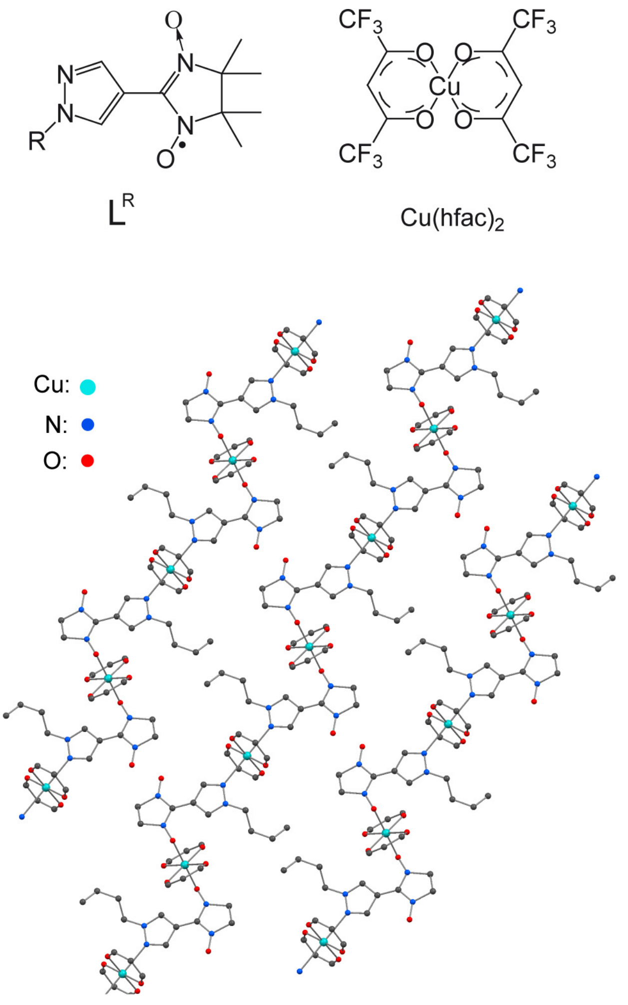


Fig. 1. Chemical structure of Cu(hfac)$_2$ and nitronyl nitroxide ligand L^R (top). Polymer-chain structure of the breathing crystal Cu(hfac)$_2$L^{Bu} (bottom). H atoms, CH$_3$ and CF$_3$ groups are omitted for clarity.

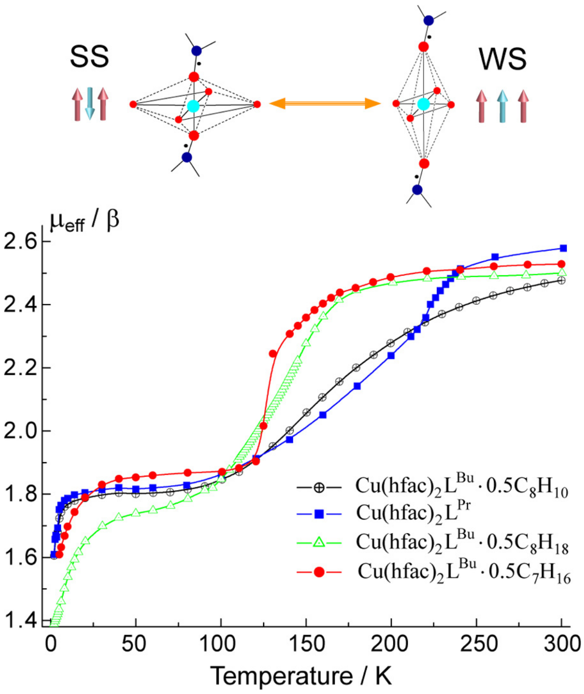


Fig. 2. Diagram of magnetostructural transitions between the weakly coupled and strongly coupled states (top). Temperature dependences of the effective magnetic moment $\mu_{eff}(T)$ for four representative breathing crystals Cu(hfac)$_2$L^{Bu} · 0.5C$_8$H$_{10}$ (Solv = orthoxylene), Cu(hfac)$_2$L^{Pr}, Cu(hfac)$_2$L^{Bu} · 0.5C$_8$H$_{18}$ (Solv = octane), and Cu(hfac)$_2$L^{Bu} · 0.5C$_7$H$_{16}$ (Solv = heptane).

It seems that these complexes have nothing in common with typical iron or cobalt-based SCO compounds. This is especially true because the electronic configuration of copper(II) (3d^9, $S = 1/2$) precludes spin state switching, and the same, of course, holds for nitroxide radical having one unpaired electron with $S = 1/2$. However, SQUID measurements have surprisingly revealed a wide variety of magnetic anomalies occurring during temperature variation in these systems (Fig. 2). These changes in the effective magnetic moment $\mu_{eff}(T)$ qualitatively resemble the behavior of SCO in iron-/cobalt-based compounds [6]. Moreover, X-ray analysis shows significant structural rearrangements in copper(II)-nitroxide units, where the direction of the elongated (Jahn–Teller) axis of the coordination octahedron changes and the complex switches between two configurations, as is shown in Fig. 2(top). Though the variation of the unit cell volume during these structural changes is noticeably large (up to ~13%), the transitions are completely reversible (both structurally and magnetically) and the crystals retain their structural integrity; that is why they were named "breathing crystals".

The above magnetic anomalies in breathing crystals are governed by exchange coupling between copper(II) and nitroxides. Note that the situation is fundamentally different in SCO compounds, where the spin state switching occurs at the level of a single transition ion and exchange interactions are generally irrelevant. The majority of breathing crystals have a polymer-chain structure in which the chains are formed according to the "head-to-head" coordination motif (Fig. 1). As a result, the polymer chains contain alternating three-spin units (or spin triads) nitroxide-copper(II)-nitroxide and one-spin copper(II) units (referred to as Cu2 units below). Magnetostructural anomalies (SCO-like behavior) occur in the spin triads and typically imply switching between two states. When the CuO$_6$ coordination octahedron is elongated along the O$_L$–Cu–O$_L$ direction and nitroxides are in the axial positions, the interspin distance is relatively large (the Cu—O$_L$ bond length is

Please cite this article in press as: M.V. Fedin, et al., Coord. Chem. Rev. (2015), http://dx.doi.org/10.1016/j.ccr.2014.11.015