



Review

Molecular magnetism, *quo vadis?* A historical perspective from a coordination chemist viewpoint☆

Jesús Ferrando-Soria^{a,*}, Julia Vallejo^{a,1}, María Castellano^{a,2}, José Martínez-Lillo^a, Emilio Pardo^a, Joan Cano^{a,b}, Isabel Castro^a, Francesc Lloret^a, Rafael Ruiz-García^{a,b}, Miguel Julve^{a,*}

^a Instituto de Ciencia Molecular (ICMol)/Departament de Química Inorgànica, c/Catedràtic José Beltrán 2, Universitat de València, 46980 Paterna (València), Spain

^b Fundació General de la Universitat de València (FGUV), València, Spain

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Dedicated to the late Professor Olivier Kahn (outstanding researcher and excellent teacher, friend, and colleague) in recognition of his invaluable contributions to molecular magnetism.

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ABSTRACT

Molecular magnetism has travelled a long way from the pioneering studies on electron exchange and double exchange or spin crossover and valence tautomerism in small oligonuclear complexes, from mono- to di- and tetranuclear species, to the current investigations about magnetic anisotropy and spin dynamics or quantum coherence of simple mono- or large polynuclear complexes, behaving as switchable bistable molecular nanomagnets for potential applications in information data storage and processing. In this review, we focus on the origin and development of the research in the field of molecular magnetism from a coordination chemistry viewpoint, which dates back to the establishment of magnetochemistry as a novel discipline among the molecular sciences. This overview is conceived as an attempt to orientate coordination chemists regarding their role in the future direction that molecular magnetism will undergo in its further evolution toward molecular spintronics and quantum computation. A particular emphasis will be given to some selected recent advances in single-molecule spintronic circuitry and quantum computing devices based on the large class of multiresponsive and multifunctional magnetic metal complexes to stimulate the progress in the field of molecular magnetism.

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* Corresponding authors.

E-mail addresses: jefeso84@gmail.com (J. Ferrando-Soria), miguel.julve@uv.es (M. Julve).

¹ Present address: EaStCHEM School of Chemistry, The University of Edinburgh, EH9 3FJ Edinburgh, UK.

² Present address: Laboratoire de Physique de la Matière Condensée, CNRS École Polytechnique, 91128 Palaiseau, France.

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1. Introduction and background

1.1. Molecular magnetism. An interdisciplinary research field

Molecular magnetism has always attracted the attention of a great number of research teams worldwide due to its multidisciplinary character [1]. Lying at the crossing point of several disciplines such as organic and inorganic chemistry, physical and materials chemistry, solid-state and applied physics, theoretical and computational physics, or bioinorganic chemistry, molecular magnetism exceeds its own field of research of magnetochemistry to include other domains of physics and biology [2,3].

Polymetallic complexes with magnetic and electronic interactions between metal centers are a major topic of molecular electronics [2] and molecular biology [3]. From a fundamental viewpoint, electron exchange and electron transfer are intimately related processes that rely on the transmission of spin- and charge-based electronic effects, respectively. The transport of electrons across relevant length scales in either nanometer-scale metal-based electronic devices [2a] or in electron-carrier

metalloproteins [3a] provides noteworthy examples of long-distance electronic coupling in artificial and natural systems, respectively. The genesis of molecular magnetism appears ligated to the study of the magnetic and electron transport properties of metalloproteins with paramagnetic metal active centers and their biomimetic (or bioinspired) model compounds, from the smaller dinuclear iron methane monooxygenase hydroxylase (MMOH) and tetranuclear iron high potential iron-sulfur protein (HIPIP) to the larger iron-oxo/hydroxo core of ferritin containing about 4500 metal ions, as depicted by Fig. 1 [3a].

In some proteins, metal centers and organic radical cofactors work in combination to carry out catalytic multielectron redox transformations of small substrates like *ortho*-thiol substituted tyrosines and *ortho*-quinone derivatives in mononuclear copper galactose oxidase (GAO) and amine oxidases (OAs) respectively, or tyrosyl radicals in the R₂ component of dinuclear iron ribonucleotide reductase (RNR R₂), as depicted by Fig. 2 [3k]. In particular, the tetranuclear manganese oxygen evolving complex (OEC) of photosystem II (PSII) in green plants and certain bacteria and algae catalyzes the four-electron oxidation of two

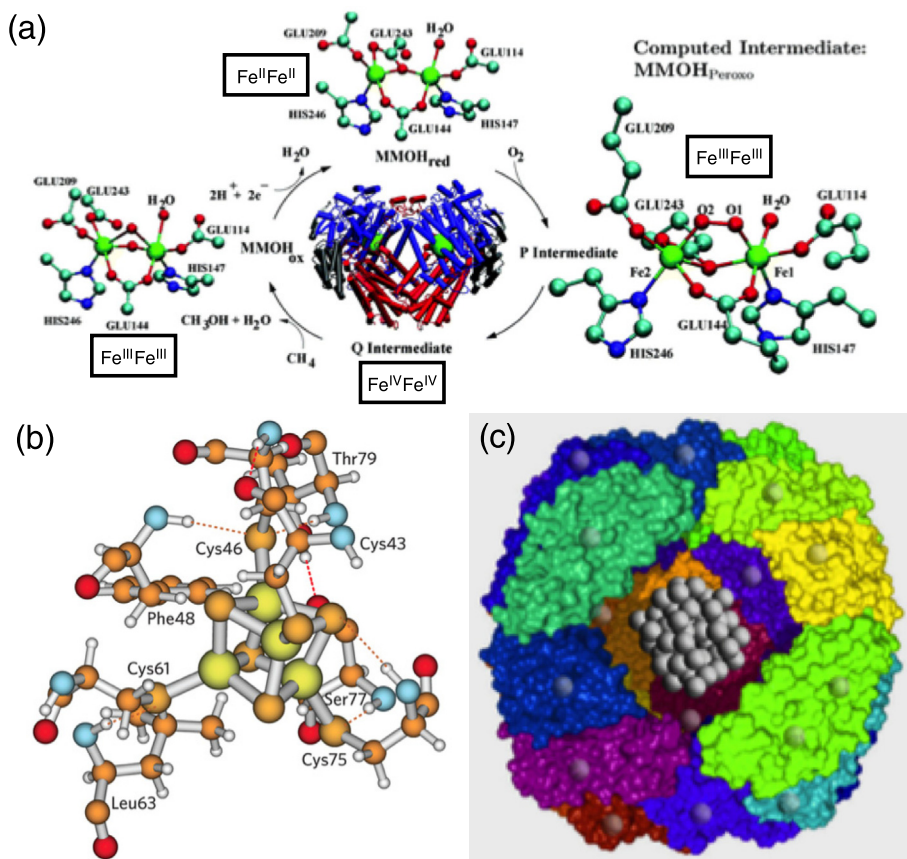


Fig. 1. Structures of the metal active site of Fe₂ MMOH (a), Fe₄ HIPIP (b), and Fe_xO(OH) ferritin (c), showing the catalytic cycle of MMOH with the proposed assignment of the metal oxidation states for the various Fe₂ intermediates. Adapted with permission from Refs. [3r,w,x].

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