



## Review

## Tetranuclear complexes in molecular magnetism: Targeted synthesis, high-field EPR and pulsed-field magnetization

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## ARTICLE INFO

## Article history:

Received 31 October 2008

Accepted 26 March 2009

Available online 5 April 2009

## Keywords:

Magnetic properties  
Oligonuclear complexes  
EPR spectroscopy  
Metalloligands  
Thiolate ligands  
Bridging ligands  
Pyrazolate ligands  
Azide ligands

## ABSTRACT

The present article reviews the synthetic approaches, the structures and the spectroscopic and magnetic properties of three different types of tetranuclear complexes: systems with metal/oximate metalloligands, tetranuclear complexes based on polydentate amine-thiophenolate ligands, and nickel/azido complexes with compartmental pyrazolate scaffolds. In all three cases, well-defined bimetallic entities have been used as building blocks for the controlled synthesis of higher-nuclearity systems. This has allowed one to modulate the magnetic properties of the tetrametallic cores and to specifically target low-spin or high-spin ground states. High-frequency high-field EPR and pulsed-field magnetization measurements have been used to experimentally determine spin Hamiltonian parameters and to probe the magnetic responses at high fields.

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## 1. Introduction

The German Research Council (Deutsche Forschungsgemeinschaft) initiated a few years ago a priority program called “Molecular Magnetism” encompassing physicists and chemists not only from Germany but also from other countries in the European Community. One of the objectives of the program was to bring together scientists from different fields, but with a common interest at magnetism of molecular species. The projects funded for six years (2002–2008) by the German Research Council were successfully completed, as illustrated here through the final reports on a variety of tetranuclear complexes by the authors. This article hopefully illustrates the value of looking at synthesis (preparative chemistry) from a molecular magnetism perspective, a lesson that obviously extends well beyond tetranuclear complexes. This review on tetranuclear complexes is expected to demonstrate also successful collaborations between different groups of chemists and physicists.

At present, the field of molecular magnetism [1] is addressing the synthesis and study of discrete polynuclear complexes in an attempt to improve our understanding of the mechanism involved in exchange coupling and the production of new paramagnetic clusters with high-spin and strong anisotropy (super-paramagnetic molecules). Exchange-coupled polymetallic complexes, in which spin coupling between paramagnetic metal ions is propagated via bridging atoms, are of special interest to researchers who seek new molecule-based magnetic materials [2]. Current emphasis lies on the targeted preparation of polynuclear transition-metal complexes with a large number of unpaired electrons in their spin ground state. This is mainly due to the fact that such compounds may behave as single-molecule magnets (SMMs) [3], that is, they can display hysteresis effects similar to those of bulk magnets but of molecular origin [4,5]. SMMs thus offer a molecular approach to magnetic materials, and their potential applications include information storage at the molecular level [6–8] and use as quantum bits in quantum computation [9–11].

Most molecule-based magnets are composed of several paramagnetic transition-metal ions, in which the metal ions are bridged via carboxylate, alkoxide, oxide, azide and cyanide bridges [12]. Many strategies have been employed over the last 25 years to obtain molecule-based magnets [13]. The use of mononuclear metal complexes of macrocyclic ligands with active coordination sites for cross-linking by suitable bridging ligands has also proven to be a very powerful strategy for the well-defined arrangement of paramagnetic transition metal ions [14–16]. Only a few groups, however, have considered higher-nuclearity complexes as building blocks for the preparation of molecule-based magnets [17,18].

It is a general phenomenon that despite the interest in the properties of exchange-coupled polymetallic systems, synthetic methods have yet to reach the level of efficiency attained with mononuclear complexes. The present contribution summarizes the results for new synthetic approaches, where well-defined binuclear complexes have been used as building blocks to assemble in a controlled fashion larger systems of higher nuclearity.

Following this general introduction related to molecular magnetism, this review article comprises three self-contained subsections. They describe the three different types of systems investigated in the author's laboratories, namely tetranuclear complexes derived from metal/oximate metalloligands (Chaudhuri/Kataev), tetranuclear complexes based on polydentate amine-thiophenolate ligands (Kersting/Kataev), and tetranuclear complexes assembled from binucleating pyrazolate-based scaffolds (Meyer/Kataev/Klauss). No attempt is made to provide a comprehensive coverage of tetranuclear complexes, the focus being mainly upon results from our laboratories.

## 2. Tetranuclear complexes from metal/oximate metalloligands

As this is a final report of the projects funded by the German Research Council (DFG), we are refraining from citing all the papers on oximate-bridged tetranuclear complexes; we will deal here mainly with our own work.

### 2.1. Synthetic strategy

Among the variety of methodologies applied to synthesize polymetallic coordination compounds, the use of “metalloligands”, i.e. metal complexes as ligands [19], in which the ligands already bound to one metal have a free lone pair of electrons for coordination to a second metal of the same or different kind, has proven to be very successful. We have favoured the strategy of “metal oximate” building blocks as ligands [20] to design and synthesize multinuclear heterometal complexes in a controlled fashion. A straightforward modular synthetic route involving metal-oximates has been developed and the concept of “metal complexes as ligands” is depicted for star-shaped and linear tetranuclear, both homo- and heteronuclear, complexes in modular form below (Scheme 1).

This section of the review deals specifically with a series of linear tetranuclear complexes containing tris(phenolato)dimanganese bridges and a Cr<sup>III</sup>Mn<sup>II</sup><sub>3</sub>-cluster that exhibits the star-shaped spin topology.

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