



Review

The bridging azido ligand as a central “player” in high-nuclearity 3d-metal cluster chemistry



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ARTICLE INFO

Article history:

Received 21 January 2014

Accepted 1 April 2014

Available online 12 April 2014

Keywords:

Azido ligand
3d-cluster chemistry
Magnetic properties
Structural analysis
SMM response

ABSTRACT

The chemistry of the azido-bridged coordination clusters continues to attract the intense interest of synthetic inorganic chemists and scientists working in the interdisciplinary field of Molecular Magnetism. In this review we have focused on describing aspects of synthesis, structures and magnetic properties of azido-bridged 3d- and d/d'-metal clusters with nuclearities equal to or higher than 4. Some of the clusters display slow magnetic relaxation at very low temperatures, mainly due to the ferromagnetic metal-metal exchange interactions propagated through the end-on azido ligand. The chemistry of polynuclear, azido-bridged 3d-metal complexes embedded in lacunary polyoxometalates is also discussed.

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1. Scope, organization of the review and general information

This review presents a focused overview of the synthetic, structural and “magnetic” chemistry of high-nuclearity 3d-metal clusters that contain bridging azido groups. Only complexes with nuclearities equal to or higher than 4 will be examined. We have searched the literature up to 2013 (CSD version 5.34 updates – May 2013). The report aims to be almost comprehensive in terms of a discussion of every discrete cluster that possesses at least one bridging azido group; in addition to bridging azide(s), most complexes contain also other inorganic or organic bridging ligands. We shall try to provide the reader with some idea of the range of chemistry that has been carried out (and indeed remains still to do) in this area. From the viewpoint of properties, the focus will be on the magnetism of the complexes; this is because the N₃⁻ ion is a key ligand in the interdisciplinary field of Molecular Magnetism [1]. Our eye on the magnetic properties of the clusters restricts the number of the metal ions whose complexes will be discussed. Organometallic clusters have been excluded from our survey.

The article contains twelve sections, including this one. The next section is introductory; the reader can find general information on the utility of molecular metal clusters in Molecular Magnetism. In Section 3 we shall give the basic features of the coordination chemistry of the N₃⁻ ion and outline its role in propagating magnetic exchange interactions between metallic spin carriers. The information in this section is essential to discuss the chemistry and magnetism of the clusters that are described in Sections 4–11 which constitute the “main menu” of this review. Sections 2 and 3 thus provide a “hors d'oeuvre” for the subsequent sections. Each of the Sections 4–9 refers to a particular metal and Sections 10 and 11 are devoted to heterometallic systems and polyoxometalates, respectively. Sections that are devoted to a single metal are divided in parts according to the nuclearity of the clusters. Section 12 provides concluding comments and the prognosis for the future.

Several review articles on azido-bridged complexes have appeared in the last 15 years or so. In 1999, Spanish scientists from Barcelona and Bilbao, including one author of the present report, described dinuclear, trinuclear, tetranuclear, and one- (1D), two- (2D) and three-dimensional (3D) Mn^{II} and Ni^{II} complexes, emphasizing structural trends and their magnetic behaviors [2]. The first review on the role of the bridging azido group as a magnetic coupler in transition metal clusters was published eight years ago [3]. The two authors, including one of us, predicted “Given the speed at which this sub-area is developing, we are acutely aware that this account will soon become outdated”; this has indeed turned out to be the case! In a broad article covering the employment of three-atom bridging ligands for the construction of magnetic molecular solids [4], Gao and co-workers commented on the utility of azides for the preparation of single-molecule magnets (SMMs), single-chain magnets (SCMs), layered weak ferromagnets and 3D porous magnets. In 2009, Stamatatos (one of the authors of this article) and Christou reviewed the employment of the N₃⁻ ion in higher oxidation state Mn cluster chemistry with emphasis on high-spin molecules and SMMs [5]. Their report demonstrated the synthetic novelty that arises when azide is used in conjunction with alcohol- and oxime-based organic ligands, the aesthetic beauty of the resulting molecules, and the often fascinating magnetic properties that these compounds possess. In a tutorial review, Bu and co-workers overviewed azido-mediated ferromagnets, ferrimagnets, canted (weak) ferromagnets, antiferromagnets, SMMs, SCMs and metamagnets [6]. The focus of the review of Adhikary and Koner in this journal three years ago was on the structural and magnetic studies of Cu^{II} clusters and coordination polymers [7]. Mukherjee and Mukherjee have recently commented on the versatility of azides for the construction of building blocks in polymeric copper(II) complexes [8]. Since some of the previous reviews deal with azido-bridged polymeric systems and due to the rapid development of the area, we believe that this work – which describes only clusters – is topical. However, overlap of information with the previous reviews will be kept to the minimum herein.

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