Review

Structural variety and magnetic properties of polynuclear assemblies based on 2-aminoglucose and tritopic triaminoguanidine ligands

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ABSTRACT

Structural features of molecular assemblies determine their magnetic properties. This has been expressed in several qualitative and quantitative magnetostructural correlations. Herein two classes of ligands and there structural and magnetic properties will be discussed. 2-Aminoglucose ligands are 2-aminoalcohols derived from a sugar backbone and therefore provide specific structural and chemical properties which can be used as structural directives. Hence, this allows to control the magnetic properties of related polynuclear complexes. On the other hand, triaminoguanidine derivatives as tritopic ligands preset an equilateral triangular arrangement of metal ions with preferentially antiferromagnetic interactions. This can be utilized to generate higher nuclearity complexes and coordination polymers.

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1. Introduction

The magnetic properties of molecular compounds have attracted considerable interest in recent years because of their relevance for the understanding of magnetically coupled active sites in metalloproteins [1]. Most recently additional interest for magnetic molecular assemblies has been generated by their potential applications as magnetic materials [2], such as magnetic memory or as building blocks in quantum devices [3]. Special attention has been devoted to polynuclear assemblies of metal ions [4], which is directly related to the search for strategies to design new systems exhibiting desired physical and chemical properties. In this context two important aspects have been emerged and intensely studied in the past: (i) how to understand and utilize magnetostructural correlations of transition-metal complexes and (ii) how to control structures of polynuclear coordination compounds.

Since the pioneering work of Bleaney and Bowers [5] researchers have been more and more concerned with the first aspect and attempted to rationalize the sign and size of magnetic couplings between metal ions on the bases of structural parameters [6]. As a result this initiated the search for qualitative or quantitative

magnetostructural correlations, which are important to understand the mechanism of interaction between metal ions [7]. The first quantitative correlation has been established for planar bis(μ-hydroxo)copper(II) dimers by Hatfield and Hodgson [8]. As in the related bis(μ-alkoxo) and bis(μ-phenoxo)copper(II) dimers, a linear relationship between the coupling constant J and the Cu–O–Cu bridging angle is observed with the latter case showing the smallest gradient [9]. Since then correlations for bis(μ-halogeno) dicopper(II) compounds [10], bis(μ-hydroxo)dichromium(III) complexes [11], bis(μ-phenoxo)nickel(II) dimers [12], μ-carboxylate-bridged dinuclear copper(II) complexes [13], dinuclear copper(II) complexes with equatorial diazine/μ-1,1-azide bridge combinations [14], dinuclear hydrogen-bridged copper(II) complexes [15], dimeric oxovanadium(IV) complexes [16], (μ-oxo)diiron(III) species [17], and face-sharing transition-metal complexes with d^3–d^3 electronic configuration [18] have been established. From these correlations a few structural parameters could be identified which determine the type and magnitude of magnetic interaction of a given system. Besides the nature of the bridging unit, these parameters include the metal–metal separation, the bond angles subtended at the bridging atoms, the dihedral angles between coordination planes containing the metal ions, the metal ligand bond lengths, and the stereochemistry of the metal ions involved.

Besides the dinuclear systems, for which detailed experimental and theoretical studies of the correlation between structure and magnetic properties have been reported in the past, there is a clear trend towards polynuclear complexes. For such systems the increased structural complexity together with the presence of different and potentially competing exchange pathways often precludes a detailed study of the exchange interactions. In addition, it should be noted here that for polynuclear complexes an over parametrization in simulations of the magnetic susceptibility data is very likely to occur, and may lead to situations were different sets of solutions similarly fit the experimental data. For larger systems this can be even paired with the limitation given by the currently available computational resources which may prevent fitting or simulation [19]. Nevertheless, in recent years also magnetostructural correlations for oligonuclear systems like mixed-bridged μ-alkoxo-μ-carboxylato trinuclear copper(II) complexes [20], tetranuclear iron(III) butterfly-type complexes [21], and M_4O_4 heterocubanes containing nickel(II) or cobalt(II) ions [22] have been reported. In particular for polynuclear systems such correlations need to be supplemented by theoretical methods based on density functional theory, which have usually been employed to calculate interaction parameters in order to compare them with experimental data and possibly to assist the selection of an appropriate set of fitted values, in case of the presence of ambiguous solutions [19]. Two rare cases of such a theoretical approach have recently been reported. The study on iron(III) butterfly-type complexes, for which a correlation between specific structural parameters and the relevant J values was found [21]. The other interesting system is given by Cu_4O_4 heterocubanes, for which the magnetic properties have been related to the number of short and long Cu$\cdots$Cu distances present in the complex and analyzed according to variations in structural parameters [23]. The two most prominent cases of Cu_4O_4 core structures, the $2+4$ and the $4+2$ class, are depicted in Scheme 1 [24].

The second general aspect of interest here, i.e. the design and construction of architectures based on metal complexes, has recently attracted considerable attention in supramolecular chemistry and crystal engineering [25]. A general approach is based on self-assembly reactions between multifunctional organic ligands and metal ions which is driven by the preference of metal ions for a particular geometry and the number, type and arrangement of the ligand binding sites [26]. This classical "node and spacer" approach [27] has led to a wide variety of supramolecular assemblies [28],
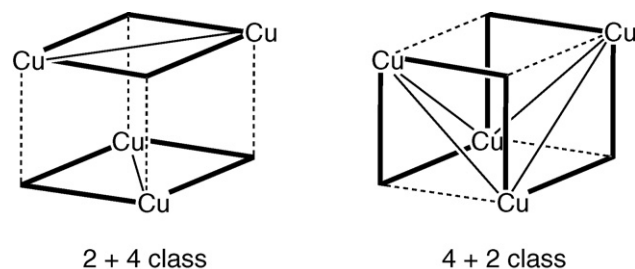
Scheme 1. Classification of tetranuclear cubane-like copper(II) complexes according the Cu–O and Cu$\cdots$Cu distances of the central Cu_4O_4 core (see text). Thick lines represent short and broken lines long Cu–O distances. Short Cu$\cdots$Cu distances are indicated by a connecting line.

ranging from oligonuclear complexes to polymeric structures with 1D chains, 2D grids, and 3D frameworks. Additional structuring options are given by the presence of hydrogen bonding interactions, as these allow to extend and cross-link relevant assemblies [29]. Nevertheless, the rational design of complexes directing a specific supramolecular assembly is still a challenge for chemists, in particular as it comes to chirality. Therefore, novel architectures with new ligands need to be synthesized to enrich crystal engineering with new connectivity rules and useful synthetic concepts. In this context metal complexes containing sugar-based salen-type ligands have recently been employed to generate homochiral helical arrays [30]. Moreover, supramolecular architectures mostly contain linear symmetric organic ligands as spacers, whereas the use of C_3 symmetric organic frameworks has been less employed [31]. However, tritopic bridging ligands with a benzene core have also been utilized to generate molecular structures [32]. Nevertheless, with respect to their magnetic properties these ligands have the disadvantage to transmit only rather small exchange couplings.

Here a brief survey is given for the latest developments concerning the generation of magnetic assemblies utilizing chiral 2-aminoglucose-based and tritopic triaminoguanidine-based ligands. The structural features of these ligand systems as well as their correlation with the induced molecular assemblies of related transition-metal complexes and their magnetic properties are discussed.

2. 2-Aminoglucose ligands as support for magnetic assemblies

2.1. Complexation behavior of 2-aminoglucose ligands

2-Aminoglucose is the monosaccharide constituting chitosan, the β-(1-4)-linked polysaccharide derived from alkaline deacetylation of chitin. Chitosan is well-known for its adsorption properties towards metal ions [33]. Its biocompatibility and non-toxicity has steamed increasing interest in this material as support and supramolecular ligand for heterogeneous catalysis [34], including Schiff-base-modified derivatives employed in cyclopropanation, alkane oxidation and C–C coupling reactions [35]. Nevertheless, the coordination chemistry of the constituting monosaccharide 2-aminoglucose (see Scheme 2) has been widely unexplored until very recently. The first reported example of a transition-metal complex exhibiting the relevant *trans*-2,3-chelation has been a tetranuclear copper(II) complex with a $4+2$ cubane-like Cu_4O_4 core (see Scheme 1) [36].

Complexes with 2-aminoglucose ligands generally tend to self-assembly affording oxo-bridged oligonuclear compounds with unexpected magnetic properties [37]. Although such a 2,3-chelation of the donor atoms of the carbohydrate backbone basically resembles that of ethanolamine, distinct differences are imposed by the rigidity and the chirality of the cyclic backbone.