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Review

Magnetism of metal-nitroxide compounds involving bis-chelating imidazole and benzimidazole substituted nitronyl nitroxide free radicals

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Contents

Abstract

Coordination compounds based on imidazole and benzimidazole substituted nitronyl nitroxide radicals with transition metal ions and trivalent lanthanide ions are described from the perspective of their magnetic properties.

For the transition metal compounds the crystal structures show various metal-nitroxide dimensionalities including mononuclear (0D), one-dimensional (1D) and two-dimensional (2D) complexes. The mononuclear complexes were isolated with most metal ions of the first transition series. One copper(II) complex shows a copper(II)–radical ferromagnetic coupling ($J = +75\ \mathrm{cm}^{-1}$) while for the other mononuclear compounds, mainly with manganese(II), the metal–radical interactions are antiferromagnetic. The one-dimensional and two-dimensional complexes are manganese(II) compounds which show canting effects leading to weak ferromagnetism.

For the trivalent lanthanide ions [La(III), Gd(III) and Eu(III)], three series of mononuclear complexes were obtained in which the metal center is bound to four, two or one nitroxide radicals depending on the counter ions and ancillary ligands. Unexpectedly, in most gadolinium(III) complexes, the Gd(III)–radical interactions were found to be antiferromagnetic in contradiction with other foundings and previous theoretical models. In support to the magnetic studies, the optical properties of the lantanide complexes have also been investigated and are briefly described.

Keywords: Nitronyl nitroxide; Complex; Copper(II); Manganese(II); Nickel(II); Zinc(II); Gadolinium(III); Europium(III); Lanthanum(III); Magnetism; Luminescence; Absorption

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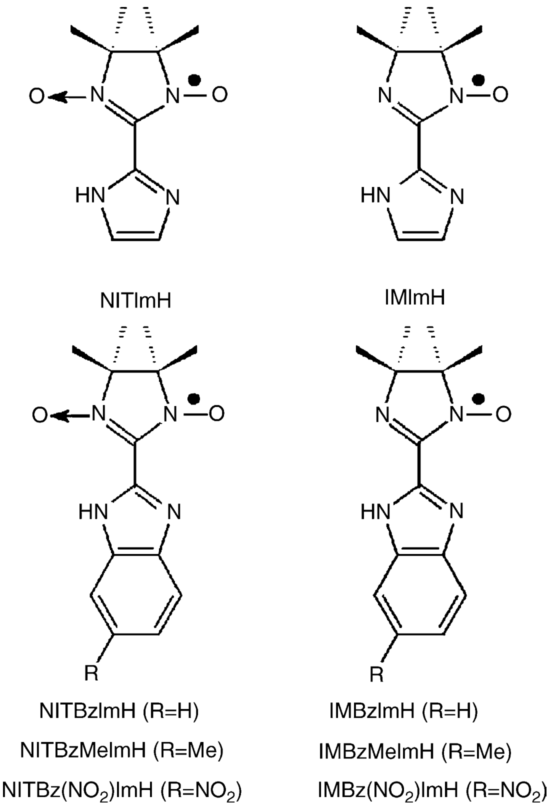
1. Introduction

From the general point of view, the strategy to get magnetic materials by coordination chemistry, relies on building extended polymetallic networks in which magnetic metal centres are connected through bridging ligands. The latters should both assemble the metal centres and mediate strong magnetic interactions, and in such a way to have a bulk nonzero magnetic moment. In this context, the use of free radicals as the bridging ligands is particularly pertinent. First, the direct bonding of the spin carriers, that is the metal centers and the free radical, should favour strong magnetic interactions. Second, the combination of inorganic and organic spin carriers allows a great versatility in the design of magnetic networks with various topologies and dimensionalities.

Whereas the metal–radical approach should not be restricted to the only nitroxide free radicals, the latter ones have gained predominance and dragged much works in the last two decades. This should be ascribed to the fact that nitroxide radicals are among the most persistent free radicals even in the presence of metal ions and may be obtained in almost limitless forms thus allowing the fine design of a large panel of magnetic bridging ligand.

The scope of the present review with respect to magnetic materials is not to cover all the results involving nitroxide–metal complexes for which some reviews have already appeared [1–5]. It concerns mostly the complexes of nitronyl or imino nitroxide grafted on imidazolyl or benzimidazolyl groups (Scheme 1) and is mainly based on our published work supported by some unpublished results.



Scheme 1.

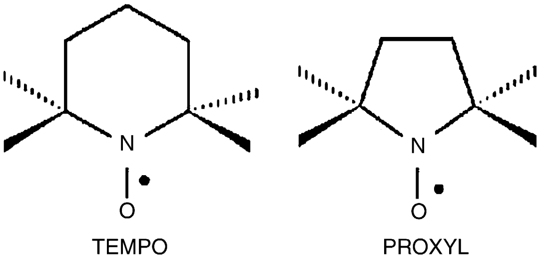
2. Background

Nitroxide free radicals are one of the best characterized groups of free radicals. Their prior interest was mainly as probes in biological systems and most of the early studies on metal-nitroxide interactions were related to this field [6]. It is in the last two decades that they became increasingly appealing as spin carriers in magnetic materials. Thus, the first organic magnets were nitroxide free radicals [7,8] and their discovery in the 1990s gave rise to extending research works dedicated to purely organic molecular based magnets [9,10].

However, the first mention of nitroxide free radical relevant to molecule-based magnetic materials was reported in the 1970s by Lim and Drago and concerned a complex in which 2,2,6,6-tetramethylpipridinyl-1-oxy free radical (TEMPO) was coordinated by the NO group [11]. This work really set up the basis of nitroxide coordination chemistry. Indeed, the main drawback of nitroxide radicals has long been the poor ability of the N–O nitroxyl group to coordinate, but in their paper Lim and Drago [11] demonstrated that it could well coordinate if a strong acidic metal centres, such as bis(hexafluoroacetylacetonato)copper(II) was used. This result was then confirmed by several other reports [12–18] which concerned complexes of copper(II) and manganese(II) acetylacetonato (hfac) or trihaloacetato ($O_2CC\ X_3$) mostly with 2,2,6,6-tetramethylpipridinyl-1-oxy (TEMPO) or 2,2,5,5-tetramethylpyrrolidinyl-1-oxy (PROXYL) [13–18] (Scheme 2) and in one case it concerned a nitronyl nitroxide radical [12]. These pioneering works were also of great relevance from the magnetic point of view as they generally demonstrated the presence of strong metal-nitroxide magnetic interactions in these systems [12,13,15,17–20].

It was Gatteschi and Rey [1,2] who first used metal-nitroxide complexes in the engineering of molecule-based magnets. Their approach was to use nitronyl nitroxide radicals as bridging ligands (Scheme 3).

Indeed, nitronyl nitroxides have two symmetrically NO groups available for coordination. Moreover, as demonstrated



Scheme 2.