

Review

Coordination effects of nitroxide radicals in transition metal and lanthanide complexes

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Abstract

The coordination effects of the magnetic interaction between a paramagnetic transition metal or lanthanide ion and radical ligand(s) upon the spectroscopic (chiroptical and/or luminescence) properties will be described and discussed mainly for the heteroleptic complexes $[M(L)(X)_2]$ ($M = \text{Ni(II)}, \text{Co(II)}, \text{Cr(III)}, \text{Ln(III)}$; $L =$ nitroxide radicals such as NIT2py(2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-3-oxide-1-oxyl) or IM2py (2-(2-(pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl), $X = \beta$ -diketonates). For the Ni(II), Cr(III) or Co(II) complexes, we show how the orbital orthogonality or overlap between the $d_{\sigma}(e_g)$ or $d_{\pi}(t_{2g})$ of the metal ion and the SOMO (singly occupied antibonding π molecular orbital) of the nitroxides is relevant to the magnetic interactions associated with the spin-forbidden d–d transition intensity enhancement and/or the newly appeared d-SOMO metal-to-ligand charge transfer (MLCT) band. This is discussed in terms of the exchange mechanism or Valence Bond Configurational Interaction (VBCI) model. From the magnetic interactions for the Cr(III) with monodentate NIT n py and IM n py ($n = 3$ or 4) and their spectroscopic properties, the appearance of MLCT state is found to be a necessary and sufficient condition for the spin-forbidden transition intensity enhancement according to the spin-polarization mechanism. The lowest excited state magnetic interaction of the Cr(III) complexes was found to be larger than that of the ground state and discussed also on the basis of VBCI model. The magnetic circular dichroism (MCD) intensity enhancement of the intraligand singlet–triplet transitions in the ancillary acetylacetonate was examined in conjunction with the ligand-to-ligand charge transfer (LLCT) for the Ni(II) complexes. The intraligand transition of the nitroxide radicals was examined in connection with the luminescence behavior of the lanthanide(III) complexes.

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1. Introduction

The magnetic and spectroscopic properties in spin-coupled systems such as multinuclear paramagnetic metal complexes or paramagnetic metal complexes with paramagnetic radical ligands have been investigated from the stand point of coordination chemistry focusing on biological and material sciences [1–12]. In biological systems, metalloproteins with polynuclear active sites and some copper metal enzymes with phenoxyl radicals such as galactose oxidase show peculiar magnetic and spectroscopic properties [9], or are relevant because of one electron oxidation centered on either the metal or ligand [10]. From the viewpoint of molecular materials leading to molecular magnets [1–8] and molecular switches including the spin-crossover phenomena [13], the transition metal clusters or complexes with nitroxide monoradicals or nitroxide–semiquinone biradicals are expected to be appropriate promising targets. The most distinctive aspects of optical spectra in the spin-exchange systems are the intensity enhancement of the spin-forbidden ligand field d–d transition in exchange coupled polynuclear or one-dimensional, two-dimensional complexes [2] and the dihydroxy bridge Cr–Cr dimers [1,15]. For example, $\text{Mn}^{\text{II}}\text{Cu}^{\text{II}}_3$ tetranuclear complexes [12] and $[\text{L}_3\text{Cr}(\text{OH})_3\text{CrL}_3]$ dimers [14] exhibit fairly strong formally spin-forbidden absorption bands. The (phenoxyl)chromium(III) complexes [10] gave too intense spin-forbidden bands to evaluate the exchange coupling constants with change of the coligand. However, there is no relevant study on nitroxide radical complexes, other than extensive magnetic studies aiming at construction of molecular magnets in terms of the so-called radical approach [6,7,16–21]. Recently, much attention has been paid to chiroptical spectra (circular dichroism (CD) and/or magnetic circular dichroism (MCD)) of the spin-coupled systems in connection with the magneto-chiral effect or chiral magnets [22]. Several CD spectra of chiral nitroxide radicals and their metal complexes have been reported [23]. It is very valuable to reveal the effect of coordination on the magneto-optical properties in order to understand the electronic spectra or the excited states of the nitroxide radical metal complexes.

Besides the magnetic interaction between the ground states in the spin-coupled systems, there are intramolecular magnetic interactions between the excited state in one moiety of the multi-spin systems and the ground state of the other one. This differentiates the excited state from the simple superposition of each moiety; e.g., the new appearance of so-called “dimer bands” due to the charge transfer (CT) transitions in Cu(II) and Fe(II) dinuclear complexes [9] and “intensity enhancement of the spin-forbidden d–d transitions” in the Mn(II)Cu(II) tetramers [12] or Cr(III) acetate trimer [24]. The former appearance of the CT is a necessary and sufficient condition to give the latter intensification in terms of a pair ion transition rather than a single ion transition [25]. The spin coupling in the excited states for the pair ion transition provides the same spin multiplicity as the ground states, leading to a formally spin-forbidden transition with the spin selection rule $\Delta S=0$ in the single group theory [12,14,15,24], but not in the double group theory through the spin-orbit coupling for the single

ion transition. In a reverse sense to the nitroxide complexes, the spin-forbidden singlet–triplet $\pi-\pi^*$ transitions of diamagnetic organic ligands is enhanced by the influence of the coordinated paramagnetic metal ion; e.g., Cr(III) [26,27]. It is useful to know whether this same framework is applicable to Ni(II) complexes in consideration of the difference in magnetic d orbitals.

Moreover, configurational interaction (CI) between the spin-coupled ground levels and the CT levels results in antiferromagnetic or ferromagnetic properties; in other words, the interaction reveals the direct mechanism, as exemplified for the metal–metal CT in polynuclear complexes by Anderson [28], and later as claimed by Weihe and Güdel [29]. This description is equivalent to the consideration in terms of the Valence Bond Configurational Interaction (VBCI) model through the LMCT and/or metal–metal transitions developed by Solomon et al. [9,30].

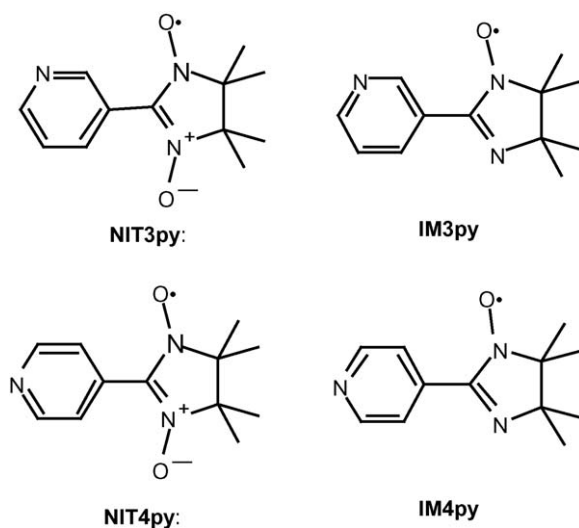
There has been no systematic study of the simultaneous observation of the spin-forbidden transition intensity enhancement and CT, with the exception of only a few cases to which the proposed theoretical formulation were applied [16]. From these aspects, we have systematically investigated the magnetic and spectroscopic properties [31–40] of a series of transition metal and lanthanide complexes with nitroxide radical ligands; these have been reviewed [41]. More recently, this research has been extended to a magneto-optical study involving the luminescence and chiroptical spectra [42–44].

In this review, the latest topics including some chiroptical spectra will mainly be highlighted and discussed on the basis of the previous results [41].

Abbreviations for ligands:

Nitroxide radicals (Scheme 1):

NIT2py: 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-3-oxide-1-oxyl,



Scheme 1.

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