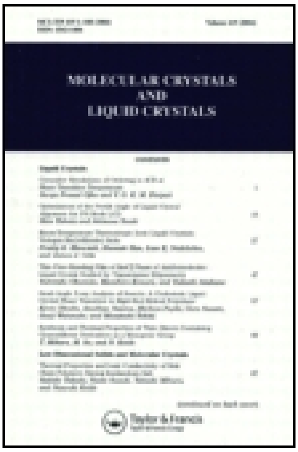

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Novel Family of Oligopyridine Based Bis-Nitronyl-Nitroxide Biradical: Coordinaton, Structural and Magnetic Properties

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NOVEL FAMILY OF OLIGOPYRIDINE BASED BIS-NITRONYL-NITROXIDE BIRADICAL: COORDINATON, STRUCTURAL AND MAGNETIC PROPERTIES

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Abstract New nitronyl-nitroxide biradicals based on 2,2'-bipyridine, 1,10-phenanthroline, 1,8-naphtyridine and 3,6-di-(2-pyridyl)-pyridazine have been synthezised and characterized. Aldehyde + hydroxylamine condensation in the presence of a catalytic amount of SeO_2 afforded, after oxidation a selective way to prepare the corresponding imino-nitroxide biradicals. Two bipyridine nitronyl-nitroxide biradicals (substituted in the 6,6' and 5,5' positions) have been characterized by a crystal structure determination. The 6,6'-substituted-2,2'-bipyridine and the 1,10-phenanthroline biradicals formed mononuclear Cu(II) and Ni(II) complexes which coordinate the two radicals to the central metal and display strong antiferromagnetic coupling at low temperature. The X-ray structures of the copper and nickel -2,2'-bipyridine-6,6'-biradical has also been determined.

INTRODUCTION

Progress in the chemistry of nitroxides was historically, largely stimulated by their use as spin labels in biological systems.[1] A considerable amount of research has been devoted to the synthesis of new stable free radicals as well as to the electronic structures of nitroxyls.[2] More recently, complexation studies with paramagnetic metals was motivated by the potential use of these complexes as molecular based magnetic materials. It is expected to attain magnetic ordering at high critical transition temperature and to generate *strong ferromagnetic* interactions.[3,4] Ligand tailoring is a powerful tool in transition metal-based magnets. Due to their manifold possibilities in fine tuning the properties of metallo-organic complexes, stable organic free radicals of the nitroxide type have been intensively studied. It is well known that by changing substituents on the radical skeleton in an organometallic compound, the different electronic and magnetic properties of the radical lead to varying magnetic behaviour.[5] Many different types of stable organic radicals have been studied, among these, one of the most popular families being the nitronyl-nitroxide radicals. Nitronyl nitroxide and imino nitroxide (Scheme 1) mono-[6,7] and bi-radicals[8] were first prepared by Ullman and co-workers. Their paramagnetic metal complexes have been extensively studied and some of these have been reported to show spontaneous magnetization, at low temperature.[9]

Scheme 1

Metal ions directly bound to nitronyl-nitroxide mono-radical as building blocks were shown to give one-dimensional ferrimagnets, ordering ferromagnetically at low temperature.[10] Many different molecular arrangements have been found by coordination of nitronyl-nitroxide free radicals to transition metal complexes (e.g. discrete molecules obtained by coordination to a single metal atom[11,12]; linear chains formed by bridging two individual metal complexes with a bidentate nitronyl-nitroxide radical[13,14] or polymeric ladder compounds formed with a tridentate nitronyl-nitroxide radical[15]; and finally discrete molecules of a cyclic manganese hexamer, with 12 coupled spins and a S = 12 ground state were also prepared[16]).

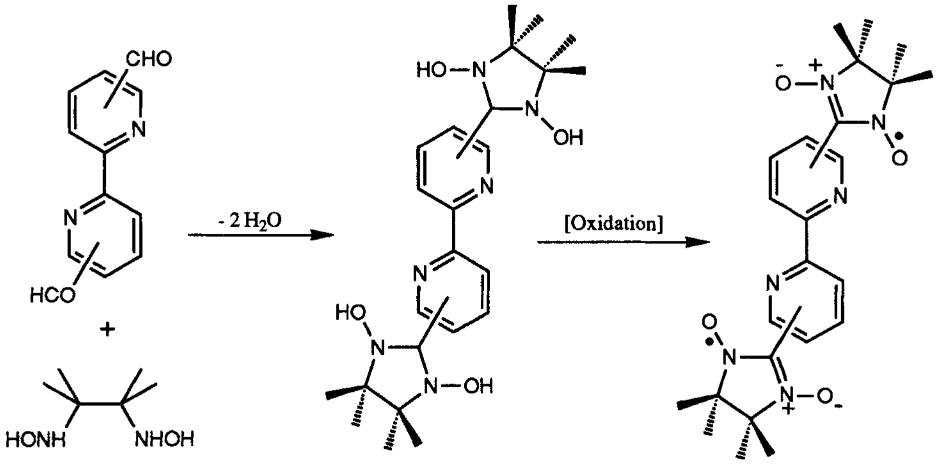
In order to obtain cooperative magnetic properties (e.g. ferromagnetism) in an organic or organo-metallic solid it is necessary not only to choose the suitable open-shell molecules, but also to orient them properly relative to each other in a three dimensional network. Specific structural modifications and chemical functionalization of stable open-shell molecules represent a challenging approach to obtain supramolecular organizations in which the natural tendency of molecules for antiparallel spin alignment is avoided. The use of hydrogen bonds as crystalline design element provides one of the most direct ways to control the relative orientation of molecules and, therefore, their electronic interactions. Depending on the position and the number of hydroxyl substituent present in the structural subunit carrying the nitronyl-nitroxide radical, the crystal packing varies, hence, inducing a great disparity in the magnetic properties of the molecular solids obtained. High dimensional organization leading to ferromagnetic intermolecular interactions has recently been achieved.[17] The formation of layered molecular materials comprising manganese and nitronyl nitroxide radicals could also be prepared by addition of an appended formyl subunit on a benzene mono-radical.[18]

As part of our interest in molecular based ferromagnetic materials, and in order to synthesize two- or ideally three-dimensional polymeric structures displaying permanent magnetization through ferromagnetic interactions, we choose two different strategies:

1) the polymerization of hybrid ligands based on oligopyridines substituted with alkynes and free radicals. As part of this project we recently developed the chemistry of polypyridine ligands functionalized by alkyne substituents.[19] Electropolymerization of some of their rigid rod-like polynuclear complexes resulted in the formation of electroactive polymeric films;[20]

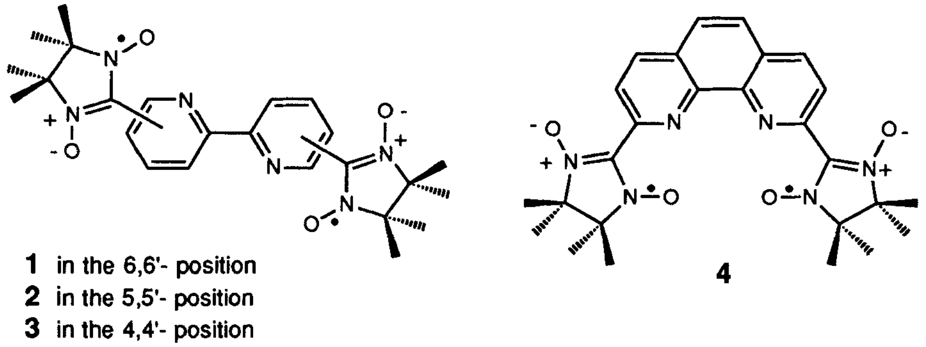
2) the use of metal complexes constructed with chelating molecules having persistent free radicals (spin carrier), as building blocks in *a complex as ligand/complex as metal* methodology.

We recently synthesized a new family of stable chelate based biradicals by a multiple (aldehyde + hydroxylamine) condensation, followed by mild oxidation under phase transfer conditions using aqueous sodium periodate or silver oxide as the oxidant (Scheme 2).[21]



Scheme 2

Depending on the relative position of the two free radicals versus the two nitrogen atoms of the 2,2'-bipyridine subunit, a great disparity of the coordination arrangements and consequently, of the magnetic properties in the molecular solids is expected. Many different monotopic biradicals have been synthesized and characterized (Scheme 3).

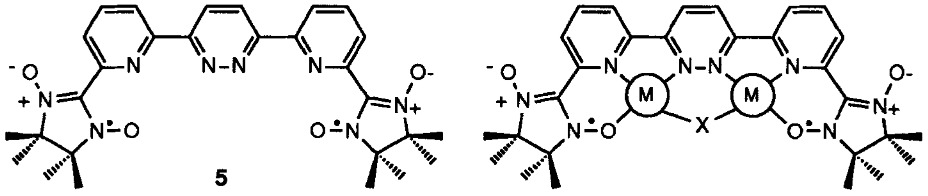


1 in the 6,6'- position
2 in the 5,5'- position
3 in the 4,4'- position

4

Scheme 3

A more rigid molecular pincer biradical **4** and a potential ditopic biradical **5** have also been studied (Scheme 4).



5

Scheme 4

All these compounds have been prepared in fair to excellent yield with the exception of compound **4** (vide supra). These very stable free radicals (decomposition observed above 220°C) show, as expected, the characteristic green to deep violet color due to n → π^* transition of aryl derivatives of aminoxylamine oxides (568 to 607 nm with ε of 350 to 740 $M^{-1}cm^{-1}$).[7,8] Magnetic moments were determined with SQUID susceptometer and lie in the range of 2.37 to 2.48 μ_B and the product of magnetic susceptibility with temperature ($\chi \cdot T$) exhibits a sharp decrease at low temperature due to intermolecular antiferromagnetic coupling between adjacent radicals. The crystal structure of two of these chelating biradicals was also determined (Figure 1). As expected the free nitronyl nitroxide biradicals **1** and **2** have a transcoide conformation of the two almost coplanar pyridine rings, and form an angle of 27.3° (for the 6,6'-derivative **1**) and of 24.2° (for the 5,5'-derivative **2**) with the mean plane of the C_5 nitronyl nitroxide cycles. These radicals were prepared by condensation of N,N'-dihydroxy-2,3-diamino-2,3-

dimethylbutane with the corresponding diformyl compounds, followed by mild oxidation under phase transfer conditions as depicted in Scheme 1.

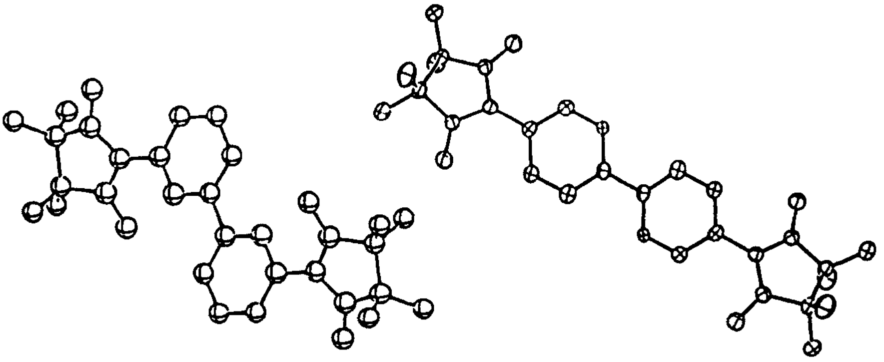
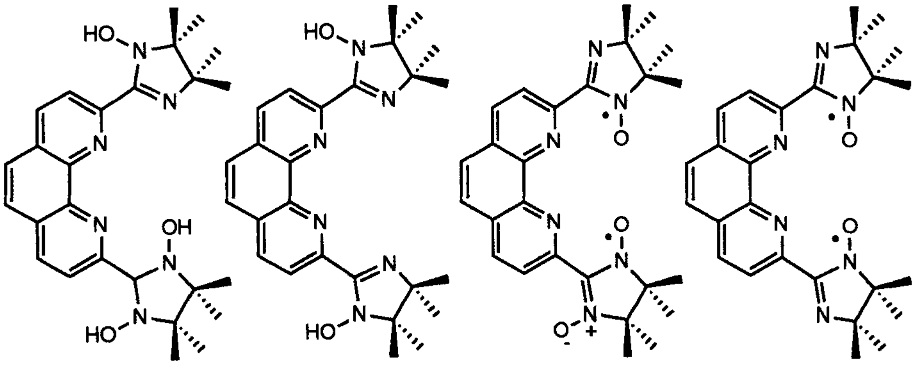


Figure 1: Molecular structure of the free bipyridine based nitronyl-nitroxide biradicals **1** (left hand side) and **2** (right hand side)

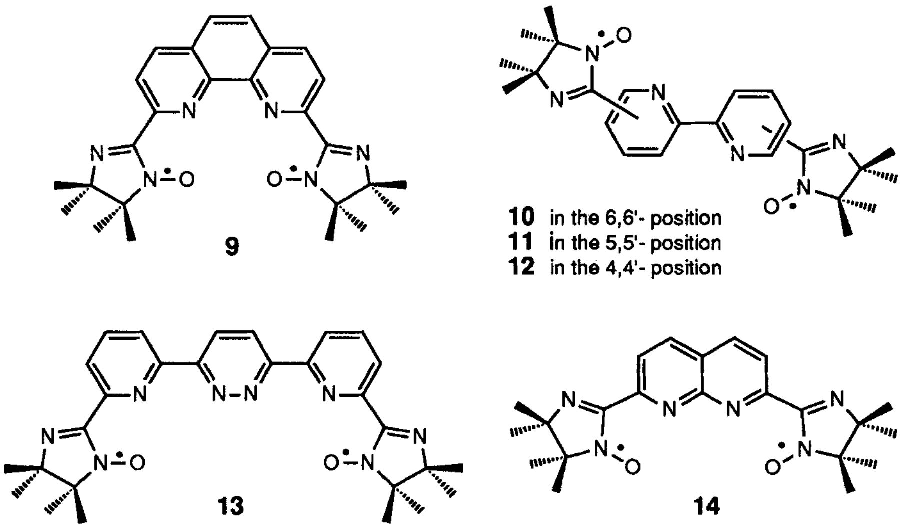
However, when 2,9-diformyl-1,10-phenanthroline was allowed to react under the same experimental conditions a yellow precipitate, identified as **6**, was formed within 2 weeks. Extending reaction time resulted in the redissolution of **6** and formation of the orange compound **7**. Mild oxidation of both species resulted in the selective formation of the mixed biradical **8** and the bis imino-nitroxide biradical **9**, respectively (Scheme 5).



6 **7** **8** **9**

Scheme 5

The presence of traces of selenium dioxide resulting from the preparation of the bis-aldehyde[22] was expected to catalyse the dehydration of the 1,3-dihydroxyimida-zolidine. Analogous results were obtained with 1,7-diformyl-2,8-naphtyridine also prepared by SeO_2 oxidation.[23] Indeed the use of selenium dioxide as a catalyst (5 mol%) in the multi-step condensation reaction is a mild and versatile method for the selective preparation of imino nitroxide based oligopyridine biradicals.[24] Imino nitroxide monoradicals are usually formed as side products during the preparation of nitronyl nitroxide radicals[7,8] and no selective method was known until now. The bis-N-hydroxyimidazolidines were prepared in good yield (40 to 90%) by multiple condensation of N,N'-dihydroxy-2,3-diamino-2,3-dimethylbutane with the formyl compounds. Mild oxidation of the bis-N-hydroxyimidazolidines under phase transfer conditions, using $NaIO_4$ gave the corresponding pure orange imino nitroxide biradicals **10** to **14** (Scheme 6).[24]

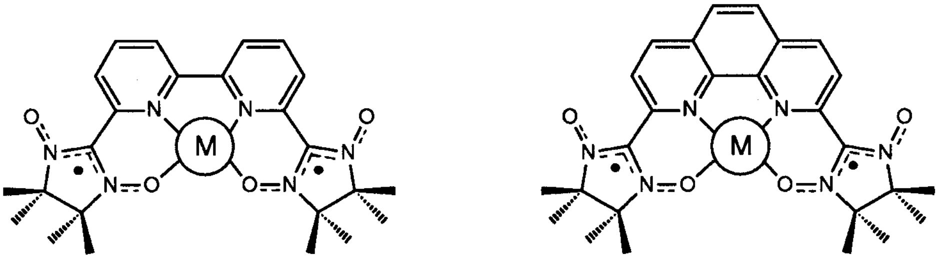


Scheme 6

Due to the very strong coordination affinities towards transition metals, oligopyridines of these two distinct series of biradicals may form very stable metal ion complexes with various structural arrangements which will provide good examples of new types of molecular based magnetic materials. Moreover, the use of a strongly acidic metal ion (e.g. hexafluoroacetylacetonate precursors) to coordinate the nitroxide to the metal centre is no longer needed. Complexation studies of ligands **1** and **4** with $Cu(ClO_4)_2.6H_2O$ or $Ni(ClO_4)_2.6H_2O$ gave the deep-green mononuclear complexes **15** and **16** (for copper) and **17** and **18** (for nickel), respectively (Scheme 7).

Interestingly the FT-IR spectra of complexes **15** and **16** display a significant shift of the NO and NC stretching frequencies. This is consistent with nitroxyl coordination to copper and has futher been confirmed by the X-Ray structure determination of complex

15 (Figure 2). Copper (II) complexation of **1** induces drastic changes in the conformation of the bipyridine (cisoide arrangement).



15 M = $Cu(ClO_4)_2$
17 M = $Ni(ClO_4)_2$

16 M = $Cu(ClO_4)_2$
18 M = $Ni(ClO_4)_2$

Scheme 7

The central Cu(II) ion is octahedrally coordinated by the bipyridine, two oxygen atoms of the two nitroxides radicals in a cis-position and two perchlorate anions in a trans-position. The bipyridine being almost planar and the C_5 cycle forms an angle of 27.9° and 19.5° with the bipyridine rings, showing little modification compared to the free ligand (Figure 1).

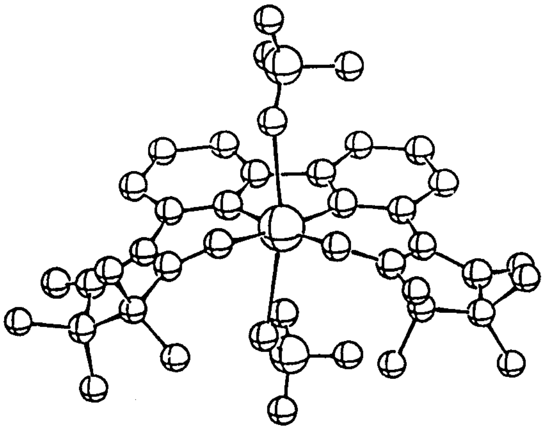
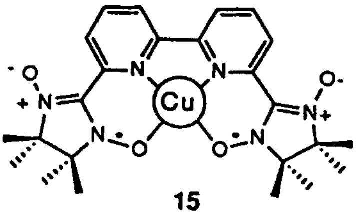


Figure 2: Molecular structure of the copper complex **15**.

Figure 3 shows the temperature dependence of the product of magnetic susceptibility with temperature ($\chi \cdot T$) for the free bipy-radical **1** (insert) and for the copper (II) complex **15**. For ligand **1**, the χ follows a Curie-Weiss law ($\mu_{eff} = 2.44\ \mu_B$ at 300 K) and exhibits a maximum at low temperature due to intermolecular antiferromagnetic coupling between adjacent radicals. Intramolecular coupling between two radicals may be ruled out because no decrease of the $\chi{\cdot}T$ value is observed at low temperature, when the bis-radical is dispersed in a glass (dichloromethane/chloroforme 1/1, 0.03 M in **1**). Similar behaviour is observed for the phenanthroline ligand **4** (μ_{eff} = 2.55 μ_B at 300 K, θ = - 1.44 cm^{-1}, see insert in Figure 3).



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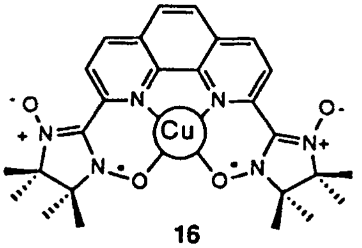

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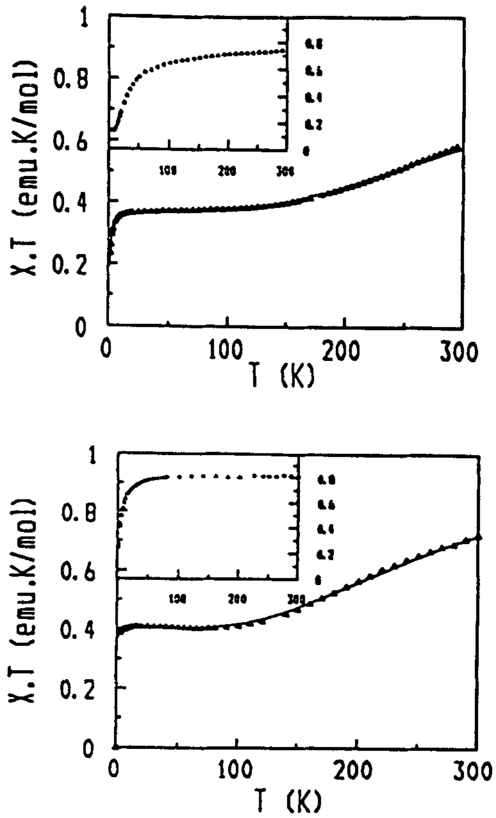

Figure 3: Temperature dependence of $\chi{\cdot}T$ for unit formula of [Cu(**1**)($ClO_4)_2$] (**15**). The solid line represents the best fit calculated values. Insert: temperature dependence of $\chi{\cdot}T$ for ligand **1** (top of the figure). Temperature dependence of $\chi{\cdot}T$ for unit formula of [Cu(**4**)($ClO_4)_2$] (**16**). The solid line represents the best fit calculated values. Insert: temperature dependence of $\chi{\cdot}T$ for ligand **4** (bottom of the figure).

For the copper complex **15**, the $\chi{\cdot}T$ product displays a continuous decrease upon cooling, from 300 to 1.7 K, as a result of antiferromagnetic couplings. At room temperature, the paramagnetic moment for three uncoupled 1/2 spins (trimer unit) is not reached ($\chi \cdot T = 0.6$ emu·K·mole^{-1}) indicating the occurance of strong intramolecular coupling. Between 120 and 13 K a nearly constant value of $\chi \cdot T$ (0.38 emu·K·mole^{-1}) is observed, in agreement with a $S = 1/2$ ground state per trimeric unit. Below 13 K, a sharp decrease of $\chi \cdot T$ is observed which is likely due to intermolecular coupling. This behaviour was analyzed by assuming strongly coupled trimeric units with a mean value of the Landé factor and a molecular field to describe the low temperature variation.[26] This model affords a radical-copper antiferromagnetic interaction $J = -168$ cm^{-1} assuming a Landé factor $g = 2.02$ and a weak intermolecular interaction related to $\theta = -0.67$ cm^{-1}.

For the phenanthroline copper complex **16** a weaker radical-copper interaction was determined ($J = -129$, $\theta = -0.07$ cm^{-1}) which might be due to a less efficient overlap of the magnetic orbitals, as a result of the rigidity of the phenanthroline chelate.

Nickel complexes of these bidentate biradicals exhibit the same structures as well as similar magnetic behaviour.[27] We are currently using these sophisticated biradicals in the synthesis of infinite molecular chains which are crosslinked by the chelating part of the biradicals. The use of hydrogen bonds to form two or ideally three dimensional structures is also ongoing in our laboratory.

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