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Synthesis of Stable Free Radicals: A Novel Family of Oligopyridine Based Nitronyl-Nitroxide Biradicals

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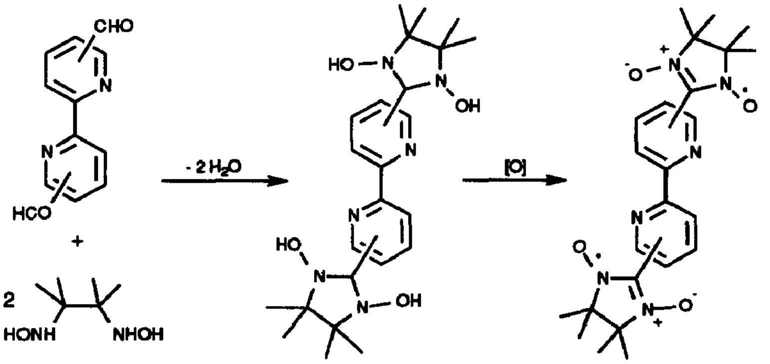
Abstract: Diformyl substituted pyridines (at the 2,5 and 2,6 positions), 2,2'-bipyridines (at the 4,4', 5,5', and 6,6' positions), 3,6-di-(6-carboxyaldehyde-2-pyridyl)-pyridazine and 2,9-dicarboxyaldehyde-1,10-phenanthroline react with *N,N'*-dihydroxy-2,3-diamino-2,3-dimethylbutane to yield the bis-*N,N'*-dihydroxyimidazolidine. Mild oxidation afforded the corresponding nitronyl-nitroxide biradicals 1 to 7. These ligands are highly colored and form very stable transition metal complexes.

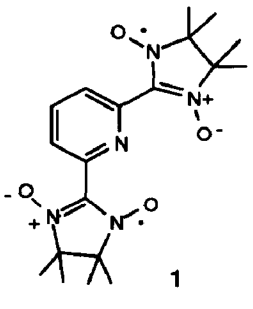
In the last decade, there has been a growing interest in the preparation of molecular based materials that exhibit cooperative magnetic properties.[1,2] One of the major challenges in this field is the synthesis of two- or ideally three-dimentional polymeric structures,[3,4] in order to display permanent magnetisation through ferromagnetic interactions. Two different strategies could be envisaged to reached this goal: (i) the polymerisation[5] of hybrid ligands based on oligopyridines substituted with alkynes and free radicals and/or (ii) the use of metal complexes, as building blocks, constructed with chelating molecules having persistent free radicals (spin carrier). As part of this project we recently developped the chemistry of polypyridine ligands functionalized by alkyne substituents.[6] Electropolymerisation of some of these ligands and their "calamitic like" complexes resulted in the formation of electroactive adherent films.[7]

In this letter we report our preliminary results on the synthesis, characterization and physical properties of a, hitherto unreported, new class of nitronyl-nitroxide based oligopyridine biradicals.



(1)

The formyl compounds, precursors of the nitroxide type radicals, were prepared using adapted literature procedures.[8] The bis-*N,N'*-dihydroxyimidazolidines were prepared in good yield by multiple condensation of *N,N'*-dihydroxy-2,3-diamino-2,3-dimethylbutane[9] with the dialdehydes.Precipitation of the product from the reaction mixture, drives the reaction towards condensation. In the pyridine, 2,2'-bipyridine and pyridazine cases the bis-*N*,*N*'-dihydroxyimidazolidines compounds were prepared in good yields. Mild oxidation of the



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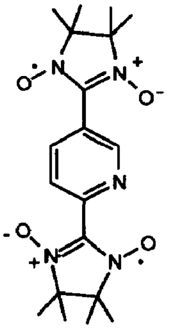

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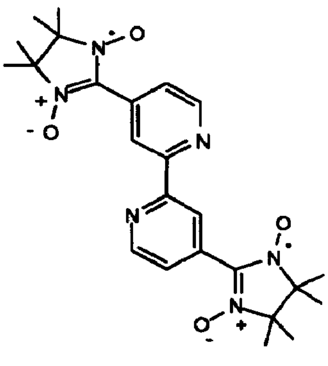

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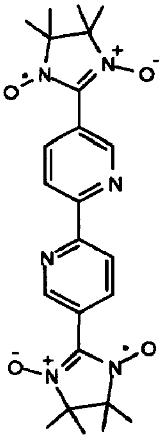

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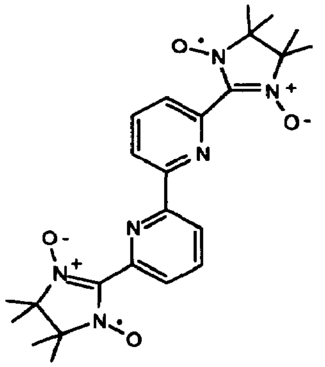

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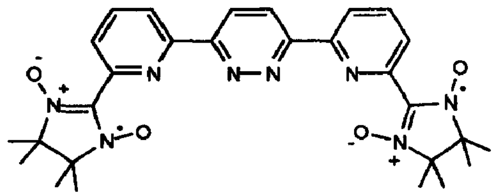

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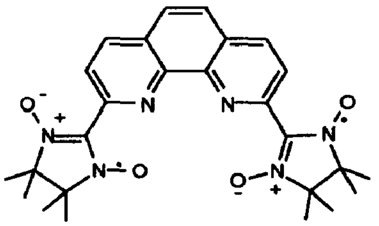

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N,*N*'-dihydroxyimidazolidines under phase transfer conditions (dichloromethane/water), at 0°C, using $NaIO_4$ or Ag_2O gave the corresponding pure deep-violet nitronyl-nitroxide biradicals **1** to **6** (after alumina chromatography and double recrystallization from dichloromethane/hexane).In the phenanthroline case the nitronyl-nitroxide biradical **7** is prepared in low yield (10%) from oxidation of the mother liquor resulting from the condensation of the diformyl with the dihydroxylamine. Oxidation of the yellow precipitate resulting from this reaction afforded a mixed mono-nitronyl-nitroxide/mono-imino-nitroxide biradical.[10]

All compounds were obtained as cristalline materials and were characterized by IR, UV-Vis, FAB+ and decomposed over 200°C. Magnetic moments were determined with a SQUID magnetometer and lie in the range of 2.37 to 2.48 μ_B. All data was consistent with the proposed structures (see Table for selected data).

Table: Selected data for compounds depicted in Scheme

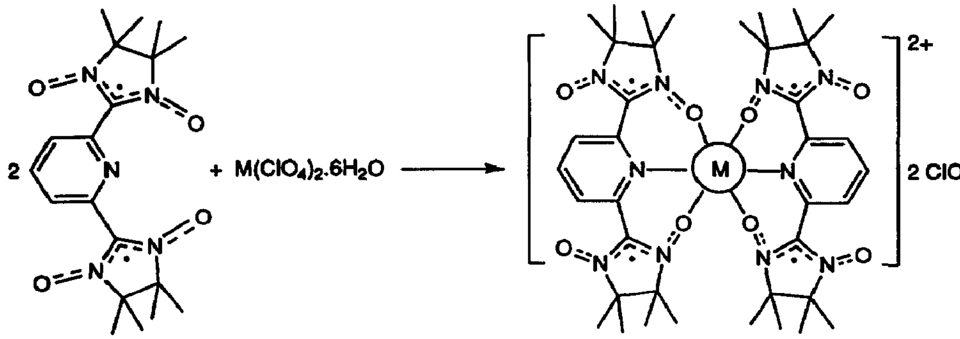
Product	Isolated yield (%)	IR ν (cm^{-1}) a)	R_f b)	UV-Vis.c) λ_{max} (nm) ε ($M^{-1}cm^{-1}$)	Mass d)
1	64	1368	0.88	570(720)	390
2	6	1351	0.82	585(550)	390
3	51e)	1345	0.63	597/530	469
4	52	1347	0.78	607(320)/532(350)	467
5	70	1358	0.65	575(740)	467
6	94	1363	0.87	574(720)	545
7	10	1354/1371	0.45	568(610)	491
8	90	1352	-	530(3170)	942/944
9	93	1343	-	575(1975)	935/937

a) ν_{N-O} (1350-1380 cm^{-1}) measured in KBr pellets except for **3** measured in CH_2Cl_2 solution; b) determined on alumina sheets in ethylacetate/methanol 95/5 except for **6** and **7** in dichloromethane/methanol 95/5; c) measured in dichloromethane; d) obtained by FAB+ using m-nitrobenzylalcohol as matrix and correspond to $[M+H]^+$, $[M+2e+3H]^+$ for **3**, $[M+2e+2H-ClO_4]^+$ for **8** and $[M-ClO_4]^+$ for **9**; e) determined by UV-Vis. absorption spectroscopy assuming an average ε value of 350 $M^{-1}cm^{-1}$ (λ_{max} 530 nm) or $\varepsilon = 320$ $M^{-1}cm^{-1}$ (λ_{max} 597 nm).

These free nitronyl-nitroxide radicals appear to be very stable and show, as expected, the characteristic dark-violet colour due to $n \rightarrow \pi^*$ transitions of aryl derivatives of aminoxylamine oxides.[11,12] The FAB+ mass spectra of the nitronyl-nitroxide biradicals exhibit an intense molecular ion peaks ($[M+H]^+$) plus characteristic major fragments due to the successive loss of oxygen atoms.

Finally preliminary complexation studies with copper(II) and nickel(II) salts shows the selective formation of a mononuclear complex with a 2/1 ligand/metal stoechiometry. These complexes have been characterized by FAB+ and microanalysis.[13] Nitronyl-nitroxide coordination to the metal is confirmed by a significant shift of the NO stretching frequency (16 and 25 cm^{-1} for the Cu(II) and Ni(II) complexes respectively). A significant hyperchromic effect of the $n \rightarrow \pi^*$ electronic transition is also observed in both complexes (see Table). X-rays structure determinations are currently under progress in order to determine the intermolecular interactions and to provide the experimental background necessary for a quantitative theoretical description of the magnetic behaviour.

The synthetic method described here allows the straightforward synthesis of new chelate based biradicals which are interesting both in their own right and as precursors for the specific synthesis of octahedral, tetrahedral and/or planar complexes transition metal complexes, which will be used in a futher step as building blocks for the controlled preparation of more extended arrays.



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8 M = Cu(II)
9 M = Ni(II)

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13. Elemental Analysis: 8 Found: C, 43.69; H, 5.17; N, 13.38, Calc. for $C_{38}H_{54}N_{10}Cl_2O_{16}Cu$: C, 43.83; H, 5.23; N, 13.45; 9 Found: C, 43.87; H, 5.09; N, 13.41, Calc. for $C_{38}H_{54}N_{10}Cl_2O_{16}Ni$: C, 44.03; H, 5.25; N, 13.51.

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