

Synthesis, Coordination and Magnetic Properties of a Novel Family of Stable Chelate Based Biradicals: Molecular Structure of a 2,2'-Bipyridine *N*-Oxide *N*-Oxyl Biradical and its Copper(II) Complex

Dominique Luneau,^a Jean Laugier,^a Paul Rey,^a Gilles Ulrich,^b Raymond Ziesel,^b Patrick Legoll^b and Marc Drillon^b

^a Commissariat à l'Energie Atomique, DRFMC-SESAM (UA 1194), Centre d'Etudes Nucléaires, 38041 Grenoble Cédex, France

^b Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg, IPCMS/GMI (URM 46), 1 rue Blaise Pascal, 67008 Strasbourg Cédex, France

Multiple (aldehyde + hydroxylamine) condensation followed by mild oxidation gives the chelating *N*-oxide *N*-oxyl biradicals **3** and **6**; both ligands gave mononuclear copper(II) and nickel(II) complexes which coordinate the two radicals and display strong antiferromagnetic coupling at low temperature.

There has been much recent interest in the synthesis of organic conductive or superconductive compounds¹, as well as in the magnetic properties of transition metal complexes prepared from stable organic radicals.² Metal ions directly bound to *N*-oxide *N*-oxyl monoradicals as building blocks have been shown to give one-dimensional ferrimagnets, ordering ferromagnetically at low temperature.^{2,3} Surprisingly, biradicals have only scarcely been studied.⁴ The recent synthesis of a pyridine based *N*-oxide *N*-oxyl monoradical⁵ prompted us to investigate the possibility of isolating some new chelate based biradicals.

Oligopyridines form strong complexes with transition metal ions, stabilizing various structural arrangements. The use of such chelating subunits in the synthesis of biradicals will (i) provide a new type of molecular-based-magnetic materials and (ii) avoid the use of a strongly acidic metal ion (e.g. hexafluoropentanedionato complexes) in order to coordinate the *N*-oxide *N*-oxyl to the metal centre.

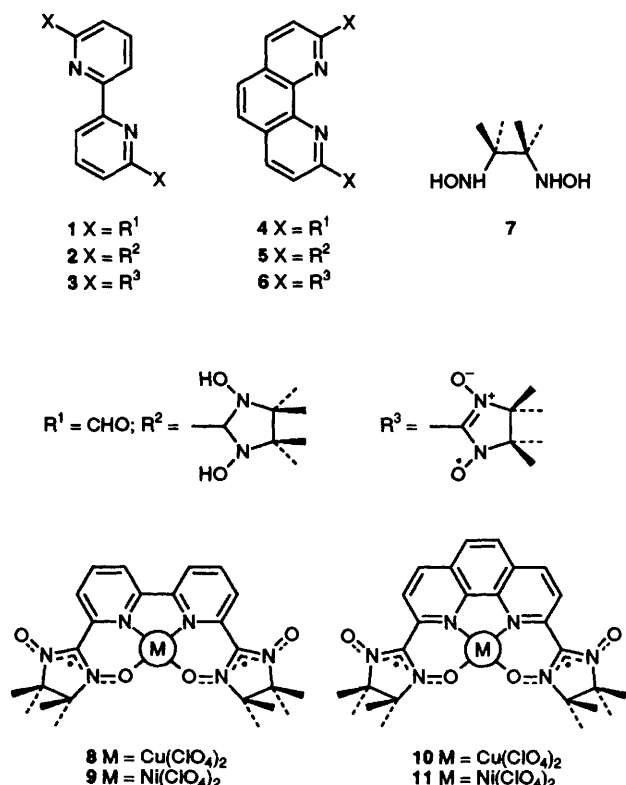
We report herein preliminary results on the synthesis, characterization and properties of the first members of a hitherto unknown family of stable bipyridine and phenanthroline based *N*-oxide *N*-oxyl biradicals (Scheme 1). The 1,3-dihydroxyimidazolidines **2** and **5** were prepared by multiple condensation of the bis-aldehydes **1**⁶ and **4**⁷ with the bis-

hydroxylamine **7**⁸ in methanol.† Oxidation of **2** and **5**, under phase-transfer conditions using aqueous sodium periodate (3 equiv.), gave the corresponding pure deep-violet *N*-oxide *N*-oxyl biradicals **3** and **6** (after alumina chromatography and double recrystallization from dichloromethane-hexane).‡ These very stable free radicals show, as expected, the characteristic dark-violet colour due to *n*→*π** transitions of aryl derivatives of aminoxylamine oxides.⁹ The FAB mass spectra of the biradicals consist of the molecular ion peaks at *m/z* 467.2 and 491.2 respectively for **3** and **6**, plus characteristic major fragments due to the successive loss of oxygen atoms.

Both biradicals may form stable metal ion complexes (Scheme 2). Indeed, complexation studies of **3** and **6** with Cu(ClO₄)₂·6H₂O gave the deep-green mononuclear complexes **8** and **10** respectively.‡ Interestingly, the FT-IR spectra of complex **8** display a significant shift (10 and 31 cm⁻¹) of the NO and NC stretching frequencies. This is consistent with *N*-oxyl coordination to copper and was confirmed by an X-ray structure determination. A related binding mode has been postulated previously in metal complexes of tetradentate bipyridine-based square-planar N₂O₂ ligands.¹⁰ Similarly, nickel(II) complexes of these ligands were prepared (complexes **9** and **11** in Scheme 2).† The crystal structures of both the free ligand **3** and its copper(II) complex **8** were determined.§ As expected, the free biradical **3** has a *transoid* arrangement of the two pyridine rings with a centre of symmetry in the middle of the bipyridine C–C bond. The two pyridine rings are coplanar and form an angle of 27.3° with the mean plane of the C₃N₂ rings (Fig. 1, top). Copper(II) complexation of **3** induces drastic changes in the conformation of the bipyridine (*cisoid* arrangement). The central Cu^{II} ion is octahedrally coordinated by the bipyridine, two oxygen atoms of the two *N*-oxyl radicals in *cis*-positions [Cu–O(1) 1.903(7) and Cu–O(3) 1.913(7) Å] and two perchlorate anions in *trans*-positions [Cu–O(6) 2.517(9) and Cu–O(10) 2.58(1) Å Fig. 1, bottom]. The bipyridine rings are almost co-planar (tilt angle of 6.4°); the five-membered rings form angles of 27.9 and 19.5° with the bipyridine rings, showing little modification compared to the free ligand.

Fig. 2 shows the temperature dependence of the product of magnetic susceptibility with temperature (*χT*) for the uncomplexed radical **3** (insert) and for the copper(II) complex **8**. In **3**, *χT* follows a Curie–Weiss law (*μ*_{eff} = 2.44 *μ*_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 a decrease in *χT* is not observed at low temperature, when the bisradical is dispersed in a glass (CH₂Cl₂–CHCl₃, 1:1; 0.03 mol dm⁻³ in **3**). Similar behaviour is observed for the phenanthroline ligand **6** [*μ*_{eff} = 2.55 *μ*_B at 300 K, *θ* = –1.44 cm⁻¹].

For **8**, *χT* decreases continuously 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 (*χT* = 0.6 emu K mol⁻¹)



indicating the occurrence of strong intramolecular coupling. Between 120 and 13 K a nearly constant value of χT (0.38 emu K mol⁻¹) is observed, in agreement with an $S = 1/2$ ground state per trimeric unit. Below 13 K, a sharp decrease of χT is apparent, probably due to intermolecular coupling.[¶] This behaviour was analysed by assuming strongly coupled trimeric units with a mean value of the Landé factor and a molecular field to describe the low-temperature variation.¹¹ 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 **10**, a weaker radical-copper interaction was determined [$J = -129$, $\theta = -0.07$ cm⁻¹] which might be due to a less efficient overlap between magnetic orbitals, as a result of the rigidity of the phenanthroline chelate. An X-ray structure determination of the nickel complex **9** is in progress in order to determine the intermolecular interactions and to provide the experimental background necessary for a quantitative theoretical description of the magnetic behaviour.

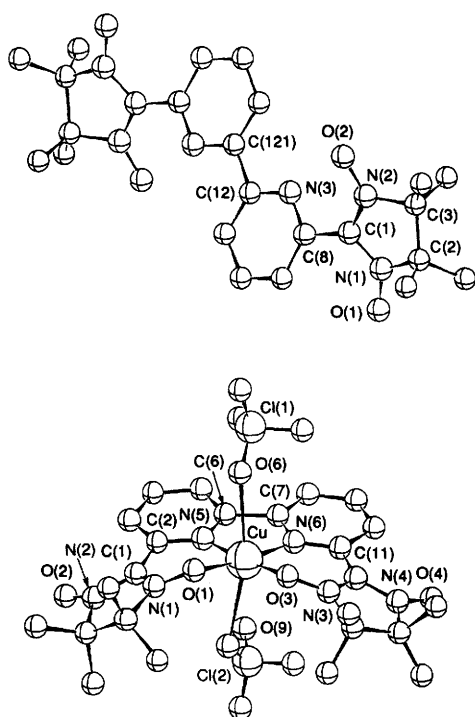


Fig. 1 Molecular structure of the free bipyridine-based *N*-oxide *N*-oxyl biradical **3** (top) and of its copper(II) perchlorate complex **8**

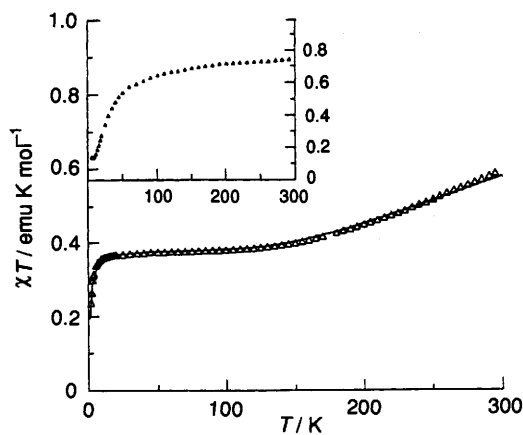


Fig. 2. Temperature dependence of χT for $[\text{Cu}(\mathbf{3})(\text{ClO}_4)_2]$ **8**. Insert: temperature dependence of χT for ligand **3**. The solid lines represent the best fit to calculated values.

Future studies of this novel series of tetradentate ligands will include complexation of rare earth metals as well as the synthesis of 5,5'-substituted bipyridine in order to prepare more extended arrays (two- or ideally three-dimensional structures).

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Footnotes

† All new diamagnetic compounds have NMR, IR, FAB⁺ and microanalytical data in agreement with their structure

‡ Compositions and structures of **3**, **6** and **8–11** were confirmed by satisfactory analytical data, IR, UV-VIS, FAB⁺ using *m*-nitrobenzyl alcohol as matrix, magnetic moments, and microanalytical analyses. Selected data are: **3**, 70%, $R_f = 0.65$, ethylacetate-methanol (95:5), Al₂O₃, mp 230–231 °C; λ/nm (CH₂Cl₂) 575, $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 740; FAB⁺ m/z 467.2 [M + H]⁺, 451.2, 436.2, 420.2, 405.2 and 336.1; ν/cm^{-1} (KBr pellet) 1411, 1358, 1181 and 1140 cm⁻¹; **6**, 10%, $R_f = 0.45$, dichloromethane-methanol (95:5), Al₂O₃, mp 194–196 °C; λ/nm (CH₂Cl₂) 569, $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 610; FAB⁺ m/z 491.2 [M + H]⁺, 475.2, 460.2, 445.2 and 360.1; ν/cm^{-1} (KBr pellet) 1410, 1370, 1165 and 1141; **8**, 68%; λ/nm (MeOH) 590, $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 650; FAB⁺ m/z 630.1 [M - ClO₄ + 2H]⁺, 614.1, 598.1, 529.2, 513.2 and 497.2; ν/cm^{-1} (KBr pellet), 1426, 1348, 1274, 1204 and 1171; **9**, 88%; λ/nm (MeOH) 755 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 642), 680, (720) and 623 (660); FAB⁺ m/z 654.0 [M - ClO₄ + 2H]⁺, 638.0, 622.0, 553.0, 537.0 and 521.0; ν/cm^{-1} (KBr pellet) 1459, 1352 and 1216; **11**, 89%.

§ Crystal data: **3**, C₂₄H₃₀N₆O₄ (from MeOH), monoclinic, $P2_1/n$, $a = 6.961(2)$, $b = 16.994(3)$, $c = 10.197(2)$ Å; $\beta = 101.15(1)^\circ$; $V = 1183.5$ Å³; $Z = 2$. Enraf-Nonius diffractometer; scan speed: 5.03 °/min, scan width 0.60 + 0.35 tan θ , $\theta \leq 25^\circ$; 2285 measured intensities, 1581 with $I > 4\sigma(I)$. Hydrogen atoms in calculated positions, anisotropic thermal parameters for all atoms except hydrogen; final $R = 4.35\%$ ($R_w = 4.68\%$). **8**, C₂₄H₃₀N₆O₄Cu(ClO₄)₂ (slow evaporation of MeOH), monoclinic $P2_1/c$; $a = 18.208(4)$, $b = 12.268(3)$, $c = 14.451(2)$ Å; $\beta = 100.63(1)^\circ$; $V = 3172.6$ Å³; $Z = 4$. Enraf-Nonius diffractometer; scan speed: 0.4–2.7 °/min, scan width 0.80 + 0.35 tan θ , $\theta \leq 27.5^\circ$; 7921 measured intensities, 2767 with $I > 4\sigma(I)$. Hydrogen atoms in calculated positions, anisotropic thermal parameters for all atoms except hydrogen; final $R = 6.0\%$ ($R_w = 7.0\%$). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ Diamagnetic contributions were estimated at -350×10^{-6} emu K mol⁻¹ from Pascal's constants (see ref. 11).

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