Pergamon

Tetrahedron Letters 40 (1999) 4543–4546

TETRAHEDRON
LETTERS

Terpyridine-based Nitroxide Radicals as New Tools for the Preparation of Magnetic Complexes

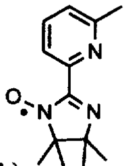
Christophe Stroh and Raymond Ziessel*

Laboratoire de Chimie, d'Electronique et de Photonique Moléculaires, associé au CNRS,
Ecole Chimie, Polymères, Matériaux (ECPM), 25 rue Becquerel, 67087 Strasbourg, Cédex 02, France

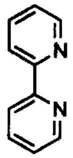
Received 30 March 1999; accepted 24 April 1999

Abstract: We report the preparation of terpyridine-like or genuine terpyridine ligands bearing appended nitronyl nitroxide (NIT) or imino nitroxide (IM) radicals. The synthetic protocol is based on multiple condensations between *N,N'*-dihydroxy-2,3-diamino-2,3-dimethylbutane and the corresponding aldehydes. Three of these radicals have been characterized by X-ray diffraction on single crystals, from which the molecular structures reveal that the five-membered radicaloid ring is significantly tilted with respect to the chelating framework. The magnetic properties of these novel mono- and biradicals are mentioned.

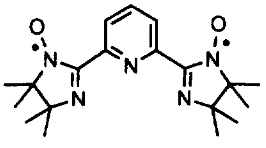
There is a continuing challenge to develop diverse sets of molecular units carrying either a free electron or a chromophoric centre for use as magnetic or optical materials. Along these lines, multifunctional oligopyridine ligands are particularly attractive because of the facile formation of complexes with most elements of the periodic table, giving rise to a rich variety of magnetic and luminophoric complexes.[1,2] The introduction of permanent free radicals into these building blocks is straightforward[3] and allows modulation of the magnetic properties of tailor-made ligands.[4] Despite the many stable radicals that have been studied to date terpyridine (terpy) chelates or terpy-like ligands grafted with nitronyl nitroxide (NIT) or imino nitroxide (IM) radicals have not been isolated before. However, a TEMPO-labelled terpy ligand has recently appeared in the literature.[5] It has also been reported that 2-methyl-6-(1'-oxyl-4',4',5',5'-tetramethylimidazoline-2'-yl)pyridine[6] (**A**) behaves as a chelate towards copper(I) in the same way as do 2,2'-bipyridine derivatives (**B**). However 2,6-bis(1'-oxyl-4',4',5',5'-tetramethylimidazoline-2'-yl)pyridine[7] (**C**, a potential tridentate ligand) seems not to behave as a classical terpy (**D**) chelate but, for redox and steric reasons, binds via the N_2O functions.[8]



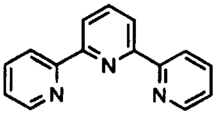
(A)



(B)



(C)

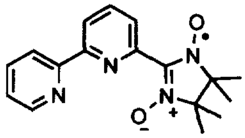


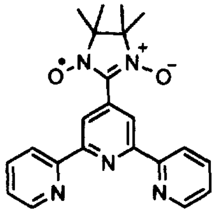
(D)

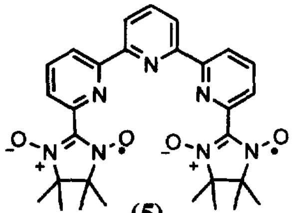
This prompted us to synthesize terpy-analogues (**1** and **2**) where one external pyridine is replaced by a nitroxide ring together with genuine terpy ligands bearing either a NIT or IM radical in the 4'-position of the central pyridine (**3** and **4**) or two such radicals in the 6 and 6" positions of the external pyridines (**5** and **6**). The target NIT molecules were prepared by multiple condensations of *N,N'*-dihydroxy-2,3-diamino-2,3-dimethylbutane with the corresponding aldehydes[9] using adapted literature procedures.[13]

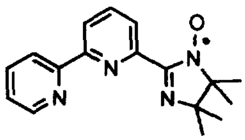
FAX: 33.3.88.13.68.95; e-mail: ziessel@chimie.u-strasbg.fr

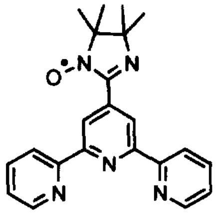
0040-4039/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(99)00805-9

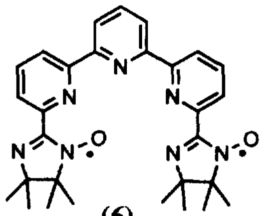

(1)


(3)


(5)


(2)


(4)


(6)

In most cases, precipitation of the resultant bis-*N,N'*-dihydroxyimidazolidine drives the reaction to completion. For the synthesis of the related IM compounds **2**, **4** and **6**, dehydration of the above intermediate to give *N*-hydroxyimidazolidine is achieved in the presence of catalytic amounts of SeO_2 (10 mol%)[7]. This pivotal intermediate does not precipitate during the reaction. In both cases, mild oxidation of the isolated intermediate (NIT case) or of the mother liquor (IM case) under phase-transfer conditions (dichloromethane/water), at rt, with $NaIO_4$ as oxidant gives the corresponding deep-blue NIT and orange-red IM radicals. Purification is achieved by alumina chromatography and recrystallization from a mixture of CH_2Cl_2 and hexane. The desired products were obtained in satisfactory yields and were characterized by FAB^+-MS, UV-vis, IR spectroscopies and elemental analysis. All data were consistent with the proposed structures (see Table for selected analytical data).

Table: Selected data for the novel radicals

Product	Isolated Yield (%)	IR (cm^{-1}) [a)]	UV-Vis λ nm, (ε, M^{-1} cm^{-1}) [b)]	MS [c)]	C; H; N Found (calc.)
(1)	61	1366	573 (340)	312.0	65.42 (65.58); 6.02 (6.15); 17.72 (17.99)
(2)	39	1373	419 (400)	296.5	68.94 (69.13); 6.22 (6.48); 18.89 (18.97)
(3)	59	1362	594 (650)	389.1	67.87 (68.03); 5.49 (5.71); 17.83 (18.03)
(4)	17	1393	449 (770)	373.1	64.55 (64.69); 6.40 (6.42); 17.09 (17.14) [d)]
(5)	39	1360	581 (560)	544.0	63.91 (64.07); 5.99 (6.12); 17.77 (18.04)
(6)	18	1374	421 (650)	512.0	67.80 (68.08); 6.20 (6.50); 18.83 (19.16)

a) ν_{NO} stretching vibration measured in KBr pellets, the $\nu_{C=N}$ stretching vibration could not preciscely be attribuated due to overlaping with other vibrations; b) n→π* absorption band measured in CH_2Cl_2; c) obtained by FAB^+ using *meta*-nitrobenzylalcohol as matrix and correspond to $[M+H]^+$; d) calculated with two water molecules.

These nitroxide radicals are relatively stable (with the exception of the IM-radical **6** upon prolongated storage) and exhibit the dark-blue colour due to n→π* transitions characteristic of aryl derivatives of aminoxylamine oxides NIT radicals.[13] Compound **2** crystallizes in the C 1 2/c1 space group, the molecular structure being shown in Fig. 1a. The dihedral angle between the radical and the [almost] planar transoid bipyridine fragment is 15°. The terpy monoradical **3** crystallizes in the P 1 2_1/c1 space group, its molecular structure being shown in Fig. 1b. The dihedral angle between the NIT radical and the central pyridine ring is 24° while the two external pyridine rings are tilted by 5 and 13°.

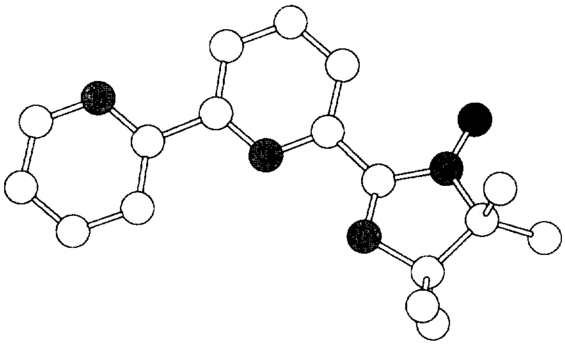


Fig. 1a. Molecular structure of **2**: selected X-ray data are: monoclinic space group, a = 29.363 (9), b = 8.209 (3), c = 12.947 (5) Å, β = 92.307 (9)°.

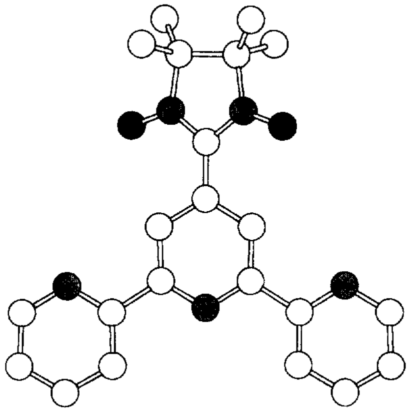


Fig. 1b. Molecular structure of **3**: selected X-ray data are: monoclinic space group, a = 14.219 (5), b = 12.913 (6), c = 11.704 (1) Å, β = 108.615 (4)°.

The terpy NIT biradical **5** is iso-structural with compound **3** and its molecular structure is depicted in Fig. 2a. Here also both radicals are tilted from the neighbouring pyridines while these external pyridines deviate from planarity by 8°. As expected for stereoelectronic reasons, the pyridine rings lie in a transoid conformation.

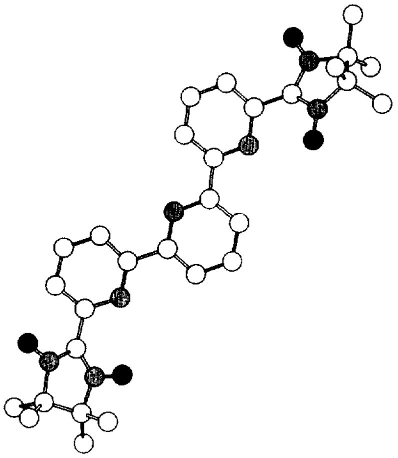


Fig. 2a: Molecular structure of **5**: selected X-ray data are: monoclinic space group, a = 7.062 (7), b = 19.370 (2), c = 20.748 (5) Å, β = 98.959 (5)°.

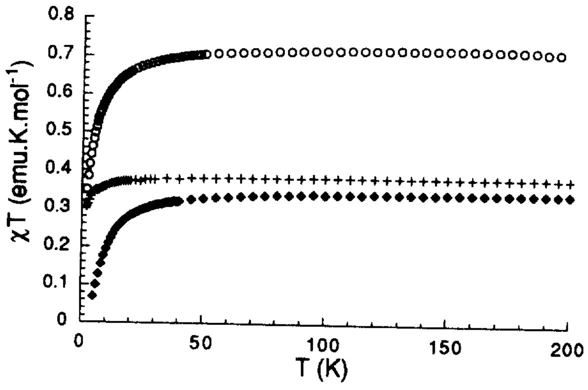


Fig. 2b: Magnetic behaviour of compounds **5** (○), **3** (✚) and **2** (◆) versus temperature.

Magnetic moments were determined with a SQUID susceptometer and lie in the range of 1.65 to 2.37 μB. The magnetic behaviour versus temperature is given in Fig. 2b for three radicals. The product of molar susceptibility and temperature (χT) at rt is in the range 0.343 to 0.377 emu•K•mol^{-1} for the monoradicals and 0.697 emu•K•mol^{-1} for the biradical. Theses values approach that expected for one or two isolated $S = 1/2$ spin systems. At low temperature, a monotonous decrease with lowering T is observed (Fig. 2b) and χ follows a Curie-Weiss law from 13 to 300 K with $\theta = -6.7$ K for compound **2**, and over the entire temperature range with $\theta = -0.5$ and -2.2 K for compounds **3** and **5** respectively. The relative orientation of two neighboring N-O subunits and the long intermolecular distance between two adjacent radicals (> 5 Å) in the crystal packing are in keeping with weak antiferromagnetic behaviour. In **5**, intramolecular magnetic interaction is excluded on the basis of previous observations made with 2,2'-bipyridine-substituted radicals dispersed in a glass-matrix.[14]

In conclusion, new chelating nitroxide-based mono- and biradicals have been prepared that contain a potential N_2N', N_2O, or N_3 chelating centre for incoming transition metal cations. The exceptional complexation properties of terpy ligands, and the ready availability of these open-shell molecules, make them ideal building blocks for preparation of octahedral and paramagnetic transition metal complexes. Extended magneto-structural correlations should provide a clear insight into the magnetic exchange pathways inherent in these systems.

References and Notes

1. Coronado, E.; Delhaès, P.; Gatteschi, D.; Miller, J. S. eds. *Molecular Magnetism: From Molecular Assemblies to the Devices* , Nato ASI Series, Vol. 321, Kluwer Academic Publishers, Dordrecht, 1996.
2. Harriman, A.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1996**, 1707-1716.
3. Ziessel, R. *Mol. Cryst. Liq. Cryst.* **1995**, *273*, 101-110 and references cited therein.
4. Luneau, D.; Romero, F. M.; Ziessel, R. *Inorg. Chem.* **1998**, *37*, 5078-5087.
5. Halcrow, M. A.; Brechin, E. K.; McInnes, E. J. L.; Mabbs, F. E.; Davies, J. E. *J. Chem. Soc., Dalton Trans.* **1998**, 2477-2482.
6. Oshio, H.; Watanabe, T.; Ohto, A.; Ito, T.; Nagashima, U. *Angew. Chem. Int. Ed. Engl.*, **1994**, *33*, 670-671.
7. Ulrich, G.; Ziessel, R. *Tetrahedron Letters* **1994**, *35*, 1215-1218.
8. Oshio, H.; Watanabe, T.; Ohto, A.; Ito, T. *Inorg. Chem.* **1997**, *36*, 1608-1610.
9. 6-Formyl-2,2'-bipyridine was prepared in quantitative yield from 6-(hydroxymethyl)-2,2'-bipyridine[10] by a Swern oxidation; 4'-formyl-2,2':6',2"-terpyridine[11] and 6,6"-diformyl-2,2':6',2"-terpyridine[12] were synthesized using described literature procedures.
10. Ziessel, R.; Lehn, J.-M. *Helv. Chim. Acta* **1990**, *73*, 1149-1162.
11. Potts, K. T.; Konwar, D. *J. Org. Chem.* **1991**, *56*, 4815-4816.
12. El-ghayoury A.; Ziessel, R. *Tetrahedron Letters* **1998**, *39*, 4473-4476.
13. Ullman, E. F.; Osiecki, J. H.; Boocock, D. G. B.; Darcy, R. *J. Am. Chem. Soc.* **1972**, *94*, 7049-7059.
14. Luneau, D.; Laugier, J.; Rey, P.; Ulrich, G.; Ziessel, R.; Legoll P.; Drillon, M. *J. Chem. Soc., Chem. Commun.* **1994**, 741-742.