Crystal Structure, Magnetic Exchange Interaction, and DFT Study of 2,2′-(1-Oxidopyridine-2,6-diyl)bis[4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-1*H*-imidazol-1-oxyl] Hydrate

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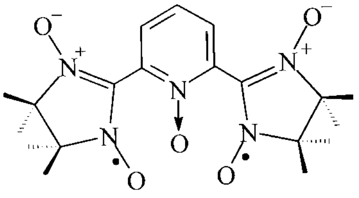
The structure of a novel oxido-aminoxyl (='nitronyl nitroxide') biradical, 2,2′-(1-oxidopyridine-2,6-diyl)bis[4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-1*H*-imidazol-1-oxyl] hydrate (**1** · H_2O) was established by X-ray analysis in the solid state: monoclinic, space group $P2_1/c$, $Z = 4$ with $a = 12.621(4)$, $b = 15.704(5)$, and $c = 13.001(4)$ Å, and $\beta = 115.202(6)°$. Variable-temperature magnetic susceptibilities show a weak antiferromagnetic interaction between the two oxido-substituted aminoxyl moieties of **1**, indicative of a singlet ground state. AM1 Calculations located minima for the possible structure based on the X-ray crystal structure. A hybride density-functional-theory calculation with the UB3LYP method from the X-ray crystal structure establishes the same spin sign in the two aminoxyl moieties and shows that a small spin density is localized at the C-atoms of the pyridine moiety. These theoretic results are in good agreement with the determined weak antiferromagnetic interaction of **1**.

Introduction. – In recent years, the study on the magneto-structural correlation has raised renewed interest among chemists and computation chemists due to its fundamental role in the design of molecular-based magnets [1][2]. Macroscopic spins in polymeric compounds containing organic free radicals are aimed towards the search for high-T_c molecular-based magnetic materials [3–5]. As is known, the critical temperature (T_c) is strongly dependent on the dimensionality of the structure and on the magnitude of the exchange interactions between spin carriers [6]. However, the donor properties of aminoxyl (= nitroxide) groups are poor [7], and this is a strong limitation for the production of a structure of high dimensionality. A strategy to overcome this limitation is to use polyaminoxyls as polydentate bridging ligands to design high-dimensional coordination compounds [8][9]. On the other hand, the study of magnetic properties of materials based on pure organic radicals has been one of the research highlights that have received much attention during the last years [10]. A number of experimental and theoretical investigations have been carried out concerning the structures and magnetic properties of *m*-xylylene (=1,3-phenylenebis[methyl])-type biradicals. These studies have contributed to the understanding of the factors governing the sign and the magnitude of magnetic exchange interactions. A spin-density and a structural rule were proposed for the design of high-spin molecules with a stable high-spin ground state [11][12]. A triplet ground state is generally expected according to the alternate polarization of the spins at π-sites of the *m*-xylylene ring based on *McConnell*'s model, but a singlet ground state is expected, according to *ab initio* calculations, when oxido-aminoxyl (= 'nitronyl nitroxide') radicals at the 1,3-positions of phenylene are twisted out of the plane of conjugation with the aromatic ring. Of *m*-xylylene-type substituted derivatives carrying two spin centers, some are found to be singlet ground states, but others to be triplet ground state. We became interested in the design of a two-spin system to investigate the magneto-structural correlation by the density-functional methods.

To extend the scope of metal-radical systems and to explore organic magnetic materials, new biradicals having two bidentate coordinating sites should be studied. In this paper, we reported the crystal structure and magnetic properties of 2,2′-(1-oxidopyridine-2,6-diyl)bis[4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-1*H*-imidazol-1-oxyl] hydrate ($\mathbf{1} \cdot H_2O$). Semi-empirical AM1 calculations show some differences in bond lengths and bond angles between the optimized and the X-ray crystal structure. Hybrid density-functional-theory calculations (DFT) based on the X-ray crystal structure were performed, leading to an excellent agreement with the experimentally suggested singlet ground state of biradical **1**.



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Results and Discussion. – *X-Ray Structure Determination of* $\mathbf{1} \cdot H_2O$. The X-ray structure determination and some crystal data are described in the *Exper. Part*. The most important bond lengths and bond angles are collected in the *Table*. The crystal structure of $\mathbf{1} \cdot H_2O$ consists of discrete molecules (*Fig. 1*). Four N–O distances in the bis-aminoxyl biradical **1** are equal within error (1.274(4) – 1.279(4) Å) and similar to the values found for other oxido-substituted aminoxyl radicals [13]. The N(1)–O(1) *N*-oxide bond length is 1.288(3) Å, close to the average N–O bond lengths (1.28 Å) of nitrone ($>C{=}N(R) \rightarrow O$) moieties, and slightly shorter than a value reported previously for a pyridine *N*-oxide complex (1.32 Å) [14]. The shortest intermolecular O$\cdots$O distance of the nitrone groups is 4.554(6) Å, which indicates very weak electronic interactions between the biradical molecules. The two five-atom fragments O–N–C–N–O are found to be nearly planar, with a deviation of less than 0.025(2) Å; they make angles of 89.6(2) and 56.7(2)°, respectively, with the pyridine plane, and an angle of 63.7(3)° with each other.

ESR Spectra and Magnetic Properties. The ESR spectra (room temperature) of the biradical **1** in CH_2Cl_2 show a nine-line pattern due to hyperfine interaction with an equivalent splitting distance of 3.8 G, which is close to half of the splitting distance in the ESR of the corresponding 3-oxido-1*H*-imidazol-1-oxyl monoradical [15].

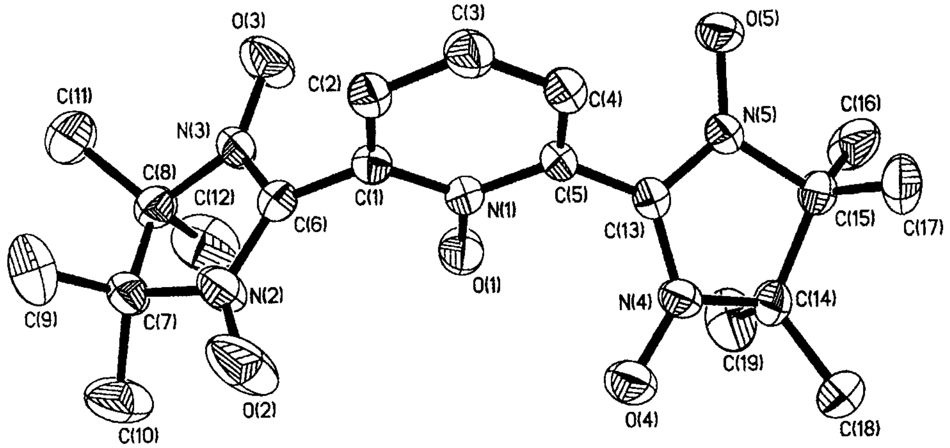

Fig. 1. *ORTEP Drawing of* **1** *with atom numbering.* Ellipsoids at 30% probability; the H_2O molecule and the H-atoms are omitted for clarity.

Table. *Experimental and Calculated* (AM1) *Structural Parameters for Biradical* **1**

	Bond length [Å]			Bond angles [°]	
	X-ray	AM1		X-ray	AM1
C(1)–N(1)	1.377(5)	1.425	C(2)–C(1)–N(1)	120.8(4)	121.1
C(1)–C(6)	1.461(5)	1.448	C(1)–C(2)–C(3)	120.6(4)	120.7
C(6)–N(2)	1.320(4)	1.422	C(2)–C(3)–C(4)	118.5(4)	119.4
N(2)–O(2)	1.275(4)	1.206	C(3)–C(4)–C(5)	120.2(4)	120.7
C(13)–N(4)	1.337(4)	1.423	N(1)–C(5)–C(4)	121.0(4)	121.1
N(4)–O(4)	1.277(4)	1.206	C(5)–N(1)–C(1)	118.9(3)	116.9
N(5)–O(5)	1.279(4)	1.209	C(1)–N(1)–O(1)	119.6(3)	121.5
N(1)–O(1)	1.288(3)	1.216	C(5)–N(1)–O(1)	121.5(3)	121.5
C(5)–N(1)	1.357(4)	1.425	C(6)–N(2)–C(7)	112.1(3)	108.9
C(5)–C(13)	1.459(5)	1.448	C(6)–N(3)–C(8)	111.8(3)	109.1
C(6)–N(3)	1.314(4)	1.421	O(2)–N(2)–C(6)	125.5(4)	125.6
N(3)–O(3)	1.274(4)	1.209	O(3)–N(3)–C(6)	124.9(3)	126.4
C(13)–N(5)	1.335(4)	1.421	O(2)–N(2)–C(7)	122.4(3)	122.3
			O(3)–N(3)–C(8)	123.0(3)	122.7
			C(13)–N(4)–C(14)	111.7(3)	108.9
			C(13)–N(5)–O(15)	111.4(3)	109.1
			O(4)–N(4)–C(13)	125.8(3)	125.6
			O(5)–N(5)–C(13)	125.5(3)	126.4
			O(4)–N(4)–C(14)	122.4(3)	122.3
			O(5)–N(5)–C(15)	122.7(3)	122.7

The temperature dependence of the magnetic susceptibility of **1** was measured in the range 1.4–300 K (*Fig. 2*) and established a $\chi_M T$ decrease on lowering of the temperature, consistent with an antiferromagnetic behavior for the two spins. The $\chi\hat{M} \sim T$ curve ($\chi_M T \sim T$) obtained for the biradical **1** was analyzed quantitatively on the basis of *Bleaney-Bowers* model ($\hat{H} = -2J_1\hat{S_1}\hat{S_2}$), including intermolecular interaction by means of a least-squares method. The parameters of the best fit were $-3.6\ \mathrm{cm}^{-1}$, 0.02 K, and 2.0 for $2J$, θ, and g, respectively. The theoretical curve is represented by the solid line in *Fig. 2*. The negative $2J$ value indicates a weak antiferromagnetic exchange interaction between two oxido-aminoxyls. A very small θ value is negligible for the intermolecular interaction in the compound. Weak antiferromagnetic interaction can be well interpreted according to the X-ray crystal structural analysis. The oxido-aminoxyl moieties are not coplanar with the pyridine ring, and the dihedral angles are larger (89.6(2) and 56.7(2)°); this is not compatible with a magnetic interaction *via* the pyridine ring.

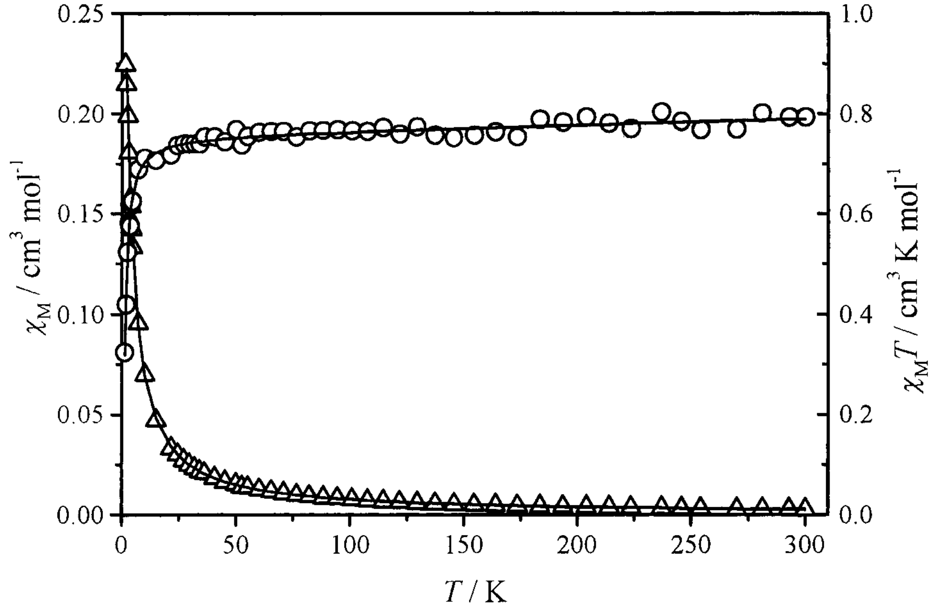

Fig. 2. *Temperature dependence of* χ_M(△) *and* χ_MT (○) *of* **1**. The solid line represents the calculated values with the best-fit parameters.

Although the calculation with the ROHF/6-31G* basis set [16] gave fairly good results for *m*-xylylene-type biradicals previously, the improvement of the basis set to UB3LYP should give an activation energy that is more accurate. We thus undertook a computational study by means of the semi-empirical AM1 and hybrid density-functional method (DFT/UB3LYP) (the 'Gaussian 94' program was used for all calculations) [17]. For simplicity, the eight Me groups of **1** were replaced by H-atoms, and the resulting model is defined as 'reduced structure'. A comparison of the bond lengths and angles of the resulting AM1-optimized reduced structure with those found for the X-ray structure of $\mathbf{1} \cdot H_2O$ (see *Table*) revealed quite large (10%) differences. The DFT calculations with the structure resulting from the X-ray analysis seemed more realistic and led to a better estimate of the electron structure.

The DFT calculations showed that the highest SOMO is mainly localized at one of the aminoxyl moieties as shown in *Fig. 3*, while the next highest SOMO is significantly localized at the pyridine moiety (*Fig. 4*). These results suggest a singlet ground state for

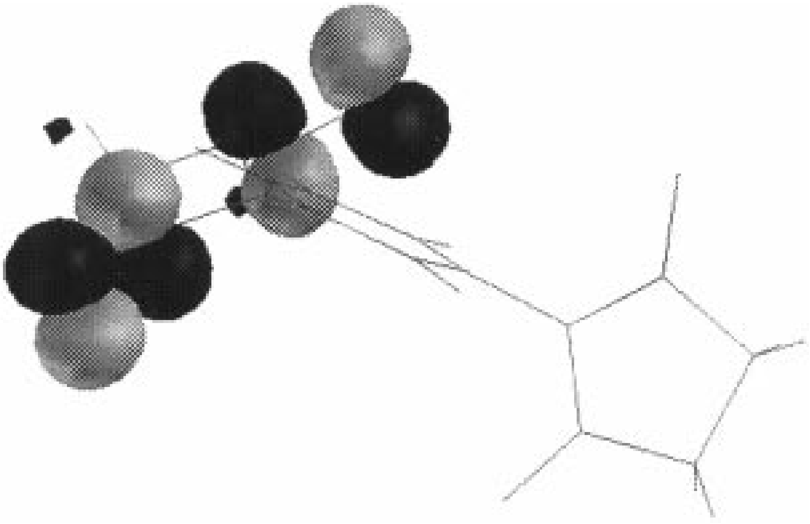

Fig. 3. *Composition of the highest SOMO orbital for* **1**

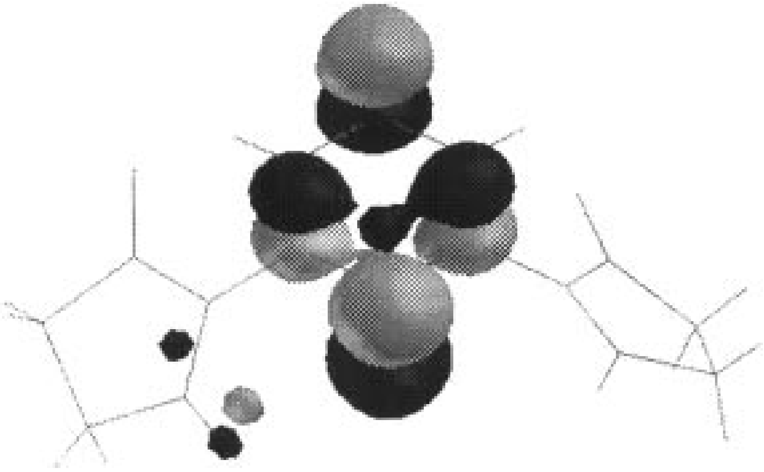

Fig. 4. *Composition of the next highest SOMO orbital for* **1**

1, according to *Hoffmann*'s theory [18] that the magnitude of the antiferromagnetic coupling interaction is directly correlated to the energy difference between the highest SOMO and the next SOMO. This result agrees well with the experimental one ($2J = -3.6\ \mathrm{cm}^{-1}$), and confirms *Rassat*'s hypothesis that an antiferromagnetic coupling is caused by the spin carriers twisted out of conjugation with the linker [18]. Furthermore, the electron spins have the same spin sign as those found for the oxido-aminoxyls, and only a small fraction of spin density is localized on the pyridine ring, as shown in *Fig. 5*. The results indicate a weak antiferromagnetic interaction between two oxido-aminoxyls, which is in agreement with the APUHF STO-3G calculation carried out previously [20].

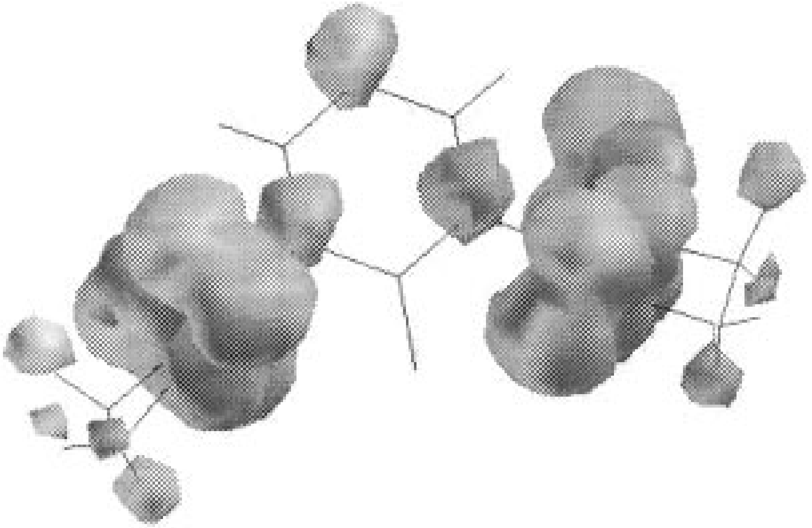

Fig. 5. *Perspective drawing of the total spin density for* **1**

Conclusion. – The magneto-structural correlation was checked for biradical **1** from both the experimental and theoretical point of view. The weak antiferromagnetic interaction is predicted by the spin density localized on the non-degenerate SOMO, as deduced from the DFT calculation based on the X-ray crystal structure. The spin density located at the oxido-aminoxyl moieties, which are twisted out of the conjugation plane of the pyridine ring, is unfavorable to a magnetic exchange interaction *via* the pyridine ring.

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Experimental Part

1. *General.* Pyridine-2,6-dicarboxaldehyde 1-oxide and *N,N'*-dihydroxy-2,3-dimethylbutane-2,3-diamine were synthesized previously according to [14][21]. IR Spectra: FT-1600 spectrameter; KBr disk; in cm^{-1}.

2. *2,2'-(1-Oxidopyridine-2,6-diyl)bis[4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-1*H*-imidazol-1-oxyl] Hydrate* **1**. A soln. of pyridine-2,6-dicarboxaldehyde 1-oxide (2.0 g, 13.2 mmol) and *N,N'*-dihydroxy-2,3-dimethylbutane-2,3-diamine (4.0 g, 27.0 mmol) in MeOH (25 ml) was refluxed for 2 h and then stirred for 5 h at r.t. After evaporation, the crude product was dissolved in CH_2Cl_2 (200 ml) and the resulting soln. oxidized at 0° for 20 min with $NaIO_4$ (4.0 g, 0.022 mmol) in H_2O (40 ml). The org. layer was washed with H_2O, dried ($MgSO_4$), and evaporated. After workup, the residue was chromatographed (neutral alumina (type III), CH_2Cl_2/MeOH 5:1): pure $\mathbf{1} \cdot H_2O$ (0.3 g, 6%). IR: 1590, 1543, 1475 (pyridine), 1354 cm^{-1} (aminoxyl), 1266, 1250 (*N*-oxide). Anal. calc. for $C_{19}H_{27}N_5O_5 \cdot H_2O$: C 53.89, H 6.90, N 16.54; found: C 53.62, H 7.25, N 16.42.

3. *Crystal Data of* **1**[1]). Dark red prismatic crystal (0.25 × 0.20 × 0.15 mm), $C_{19}H_{27}N_5O_5 \cdot H_2O$, M_r 423.47; monoclinic, space group $P2_1/c$, $a = 12.621(4)$, $b = 15.704(5)$, $c = 13.001(4)$ Å; $\beta = 115.202(6)°$; $V =$

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[1]) Crystallographic data (excluding structure factors) have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-141953. Copies of the data can be obtained, free of charge, on application to the CCDC, 12, Union Road, Cambridge CB21EZ, UK (fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

2331.6(12) Å^3, $Z = 4$, $D_c = 1.206$ mg · m^{-3}; MoK_α radiation: $\lambda = 0.71073$ Å, $\mu = 0.091$ mm^{-1}. *Bruker Smart-1000* area diffractometer with a graphite monochromater, 293 K. In the range $3.21° \leq \theta \leq 25.5°$, 9407 reflections were collected, 4058 reflections being independent. The *Siemens* area detector absorption program (SADABS) was used for absorption correction [22]. $T_{\min}$ and $T_{\max}$ for the SADABS correction were *ca.* 0.9776 and 0.9865, resp. The structure was solved by standard methods, and full-matrix least-squares refinements based on F^2 were performed with non-H-atoms assigned anisotropic thermal parameters. There is a H_2O molecule and the biradical molecule **1** in the asymmetric unit. The H-atoms of this H_2O were not included in this model, and the others were found by difference *Fourier* syntheses with isotropic thermal parameters and constructed in geometrically reasonable positions. There are two voids of 125 A$^{\circ 3}$ volume per unit cell, and these were calculated with the aid of the coordinates of the full model. These voids are not occupied by H-atoms because 108 of the 116 per unit cell have already been taken into account in the calculation of the volume occupied by the molecules. It is possible that some solvent molecules left the lattice, and that the crystal remained a stable structure containing empty space of that magnitude. Programs from the *Siemens* SHELXS and SHELXL, together with the program package Platon (A.L. SPEK 2000), were used for the calculation and refinement [23]. A total of 271 parameters were refined, so that a data-to-parameter ratio of 15.0 resulted. The final R_1 and wR_2 values for data with $I > 2\sigma(I)$ were 0.0673 and 0.1210. The goodness-of-fit based on F^2 was 0.946. The final difference *Fourier* maps had peak maximum and minimum at 0.223 and -0.170 eÅ^3.

4. *Molecular-Orbital Calculations.* The molecular-orbital calculations were done by the semiempirical method, and the spin-density calculations were performed by the hybrid UB3LYP method proposed by *Becke* [24].

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