A Diradical Bridging Ligand with a Triplet Ground State

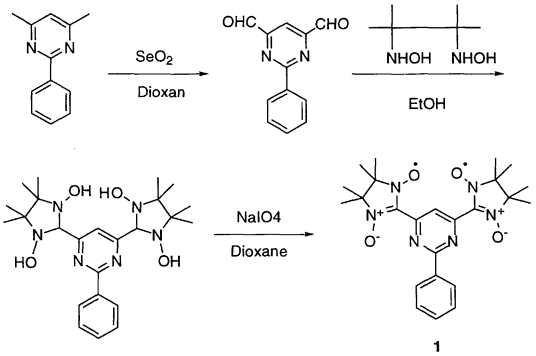
Hiroki Oshio,* Makoto Umeno, Toru Fukushi, and Tasuku Ito
Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-77

(Received July 14, 1997; CL-970552)

A diradical of nitronyl nitroxide, 2-phenyl-4,6-bis(1'-oxyl-3'oxido-4', 4', 5', 5'-tetramethyl-4',5'-dihydro-1'H-imidazole-2'-yl)pyrimidine, was prepared and characterized to have a triplet ground state.

There has been increasing interests in molecular based magnetic materials. In the rational development of new magnetic materials, control of local spin-spin interactions is crucial. Studies of organic diradicals revealed that spin polarization in delocalized and planar π-systems with appropriate topologies leads to the ferromagnetic interaction,[1] and this mechanism was applied to the synthesis of organic high-spin systems[2] and to ferromagentically coupled metal complexes.[3] On the other hand, metal complexes with nitronyl or imino nitroxides have shown a variety of magnetic behavior such as strong ferromagnetic interactions and magnetic ordering.[4] Many efforts have been, therefore, devoted to synthesize poly-radicals having macroscopic spin alignment with the aid of complexation with metal ions.[5] Here we report synthesis and magnetic properties of diradical bridging ligands with the triplet ground state. The bridging ligand prepared has two nitronyl nitroxides linked to the pyrimidine with a meta-position, and in a bridged complex metal ions are also expected to have the ferromagnetic interaction by means of the spin polarization of the intervening dπ-spins to the pyrimidine pπ-orbitals.

2-Phenyl-4,6-pyrimidine-di-carboxyaldehyde **1**, which was prepared by the oxidation of the corresponding dimethyl compound, was condensed with 2,3-hydoxyamino-2,3-dimethyl-n-butane, and the resulting bis(hydroxylamine) was oxidized with $NaIO_4$ to give diradical **1**.[6]



1

Recrystallization from CH_3Cl gave dark green tablets and one of them was subjected to the X-ray analysis.[7] Ortep diagram of **1** was depicted in Figure 1. Bond lengths of N-O are 1.258(6) - 1.277(5) Å, which are characteristic of nitroxides. Pyrimidine ring is almost coplanar (3.8(2)°) with the phenyl ring, but forms angles of 27.5(2) and 20.5(2)° with the planes of the nitronyl nitroxide O-N-C-N-O. The dihedral angles of the two nitronyl nitroxides in the molecule is 27.8(6)°.

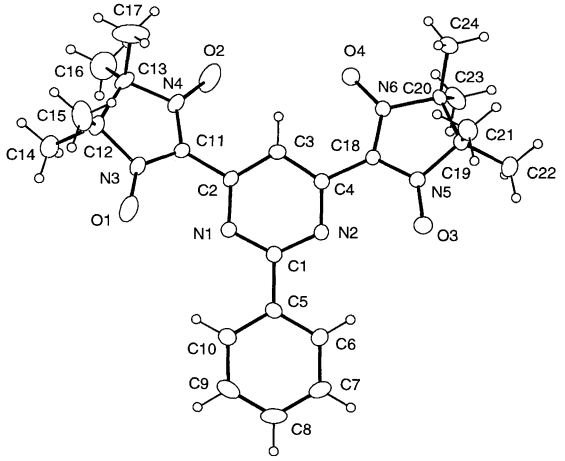


Figure 1. ORTEP diagram of **1** with 30 % probability ellipsoids.

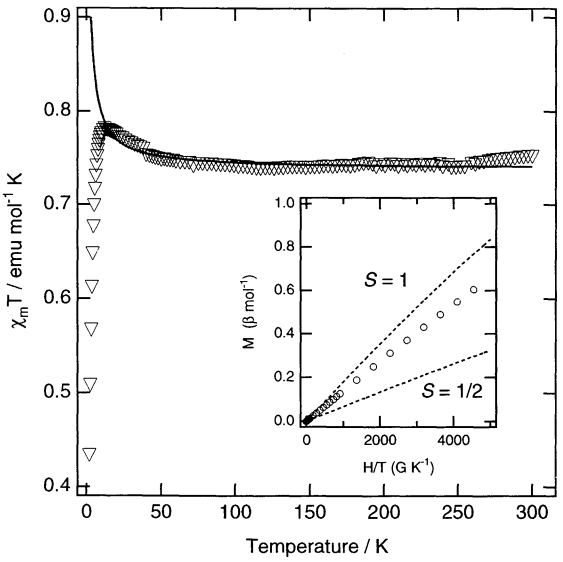


Figure 2. Plots of $\chi_m T$ versus T and mangetization versus field strength of **1**. Solid and dotted lines correspond to the best fit curve by using the the Bleaney-Bowers equation and the Brillouin functions with S =1/2 and 1, respectively.

The magnetic susceptibility data of **1** are shown in the form of the $\chi_m T$ vs. T plot, where χ_m is the molar magnetic susceptibility (Figure 2). The $\chi_m T$ value at 300 K is 0.75 emu mol^{-1} K which would be expected for uncorrelated two spins. As the temperature is lowered, the $\chi_m T$ values shows a gradual increase, reaching the maximum value (0.78 emu mol^{-1} K) at 11 K, and then decreases. The structural analysis showed that the oxygen atom (O2) of the nitroxide has the closest interatomic contact (3.45(1) Å) with the oxygen atom. The close contact of the nitroxyl group implies SOMO-SOMO overlap and this leads to the intermolecular magnetic interaction being antiferromagnetic. The magnetic behavior was, therefore, analyzed by assuming the intramolecular ferromagnetic interaction being operative in the intermediate temperature. The least squares fitting for the data above 11 K gives the best fit parameters $2J$ and g values of 2.4(1) cm^{-1} and 1.99(1), respectively, by using the Bleaney-Bowers equation ($H = -2JS_1 \cdot S_2$).[8] Magnetization experiments at 11 K showed that the experimental magnetization values are greater than the value predicted by the Brillouin function for S = 1/2 (Figure 2). An X-band epr spectrum of a frozen ethanol solution at 77 K (Figure 3) gave a fine structure characteristic of the triplet signal and zero-field splitting parameters of $|D/hc|$ and $|E/hc|$ were determined to be 0.010 and 0.002 cm^{-1}, respectively.

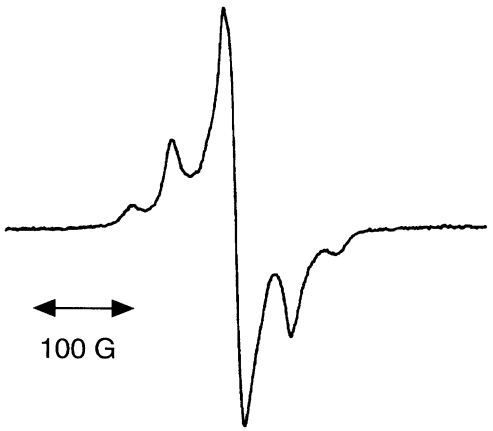


Figure 3. X-band epr spectrum of a frozen ethanol solution of **1** at 77 K

The present compound provides us with an example of spin polarization mechanism being useful for preparing the bridging ligand with a high-spin ground state. Attempts to prepare multinuclear complexes toward high-spin molecule or magnetically ordered complexes are under way.

References

1 a) H. M. McConnel, *J. Chem. Phys.*, **39**, 1910 (1963). b) J. Higuchi, *J. Chem. Phys.*, **38**, 1237 (1963).

2 a) K. Ito, *Chem. Phys. Lett.*, **1**, 235 (1967). b) T. Sugawara, S. Bando, K. Kimura, H. Iwamura, and K. Itoh, *J. Am. Chem. Soc.*, **108**, 368 (1986).

3 H. Oshio and H. Ichida, *J. Phys. Chem.*, **99**, 3294 (1995).

4 a) H. O. Stumph, L. Quahab, Y. Pei, D. Grandjean, and O. Kahn, *Science*, **261**, 447, (1993). b) A. Caneschi, D. Gatteschi, J. P. Renard, P. Rey, and R. Sessoli, *Inorg. Chem.* **28**, 1976 (1989). c) K. Inoue and H. Iwamura, *J. Am. Chem. Soc.*, **116**, 3137 (1994). d) H. Oshio, T. Watanabe, A. Ohto, T. Ito and U. Nagashima, *Angew. Chem. Int. Ed. Engl.*, **33**, 670 (1994).

5 T. Mitsumori, K. Inoue, N. Koga, and H. Iwamura, *J. Am. Chem. Soc.* **117**, 2467 (1995).

6 Anal. Found: C, 61.30; H, 6.42; N, 18.13%. Calcd for $C_{24}H_{30}N_6O_4$: C, 61.79; H, 6.48 ; N, 18.01%.

7 Crystal data: $C_{24}H_{30}N_6O_4$ **1**: M = 466.54, monoclinic, space group $P2_1/n$, a = 6.299(5), b = 17.988(5), c = 20.786(5) Å, β = 93.78(5)°, V = 2350(2) $Å^3$, Z = 4, D_C = 1.32 g cm^{-3}, T = 213 K. A single crystal of **1** was mounted on a glass fiber with epoxy resin. The minimum and maximum transmission factors were 0.98 and 1.00. The structure was solved by direct methods with SHELX-86 (G. M. Sheldrick, University of Göttingen, 1986) and Fourier techniques, and refined by full-matrix least-squares on F^2 using SHELXL-93 (G. M. Sheldrick, University of Göttingen, 1993). All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. Hydrogen atoms were located on calculated positions and were refined by the riding model. The refinement of 307 parameters converged to $R(F)$ = 0.071 and R_w (F^2) = 0.142 (for 1965 reflections with $I_0 > 2\sigma(I_0)$).

8 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A* , **214**, 451 (1952).