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α-Nitronyl Nitroxide Cation Radicals

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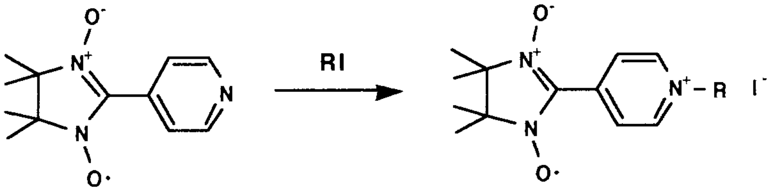
X-Ray crystal analysis and magnetic measurements have been carried out on the first *cation* radical salt of α-nitronyl nitroxide, 2-(4-*N*-R-pyridinium)-4,4,5,5-tetrametyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-*N*-oxide iodide (with R=methyl (**1**) and ethyl), suggesting the separation between the spin and the charge density population, and revealing the strong antiferromagnetic intermolecular interaction of J_{AF}/k_B=149 K in **1**.

A free radical family, α-nitronyl nitroxide, is attracting the interests from the view point of the organic/molecular ferromagnetism.[1-5] We report the structure and magnetic properties of the first α-nitronyl nitroxide *cation* radical. The cation radicals were prepared by the *N*-alkylation of 4-pyridine-α-nitronyl nitroxide.[6] The iodide salts, 2-(4-*N*-R-pyridinium)-4,4,5,5-tetrametyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-*N*-oxide iodide (with R=methyl (**1**) and ethyl (**2**)), were separated from the solutions of the pyridine derivative in the alkyl iodides. **2** crystallized with water in the solvent or in the air as $(\mathbf{2})_2 \cdot H_2O$, while **1** did not include crystal water. The elemental analyses gave C, 41.35; H, 5.00; N, 11.29 (theory C, 41.50; H, 5.09; N, 11.17) for **1** and C, 42.51; H, 5.32; N, 10.59 (theory C, 42.12; H, 5.55; N, 10.52) for $(\mathbf{2})_2 \cdot H_2O$. The IR spectra of **1** and **2** clearly showed the difference due to the crystal water.



R = **-CH$_3$ (1) and -C$_2$H$_5$ (2)**

A single crystal of **2** suitable for X-ray diffraction studies was grown by the standing of the above ethyl iodide solution in the air. Crystal data and the experimental conditions for the X-ray analysis are as follows:

$C_{14}H_{21}N_3O_2I \cdot \frac{1}{2}H_2O$, green, M=399.25, triclinic, space group $P\bar{1}$, a=12.582(6), b=13.633(8), c=11.120(6) Å, α=93.31(4), β=115.47(2), γ=88.91(4)° at room temp, U=1719(2) Å^3, Z=4. Data with $2<2\theta<60°$ were collected on a ENRAF NONIUS CAD4 four-circle diffractometer with monochromatic Mo-K_α radiation. $R(F)$=0.085 for 5241 independent reflection with $|F_o|>3\sigma(F_o)$. The single-crystal growth of **1** was unsuccessful.

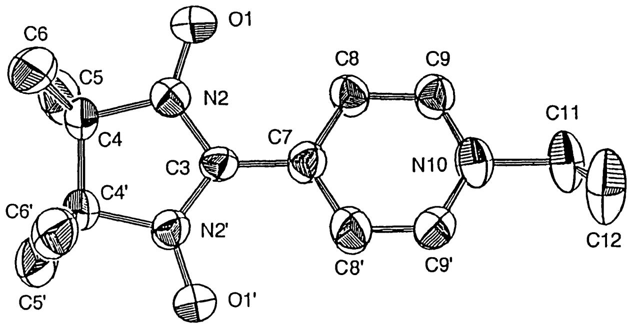


Fig. 1. Atom numbering scheme and molecular conformation of **2A**. Selected interatomic distances (Å) and angles (°): O1-N2 1.273(10), N2-C3 1.356(10), C3-C7 1.442(15), C7-C8 1.377(13), C8-C9 1.394(16), C9-N10 1.328(12), N10-C11 1.515(17); O1-N2-C3 126.3(9), N2-C3-N2' 108.2(9), C8-C7-C8' 117.9(11), C7-C8-C9 120.6(8), C8-C9-N10 119.6(9), C9-N10-C9' 121.6(10).

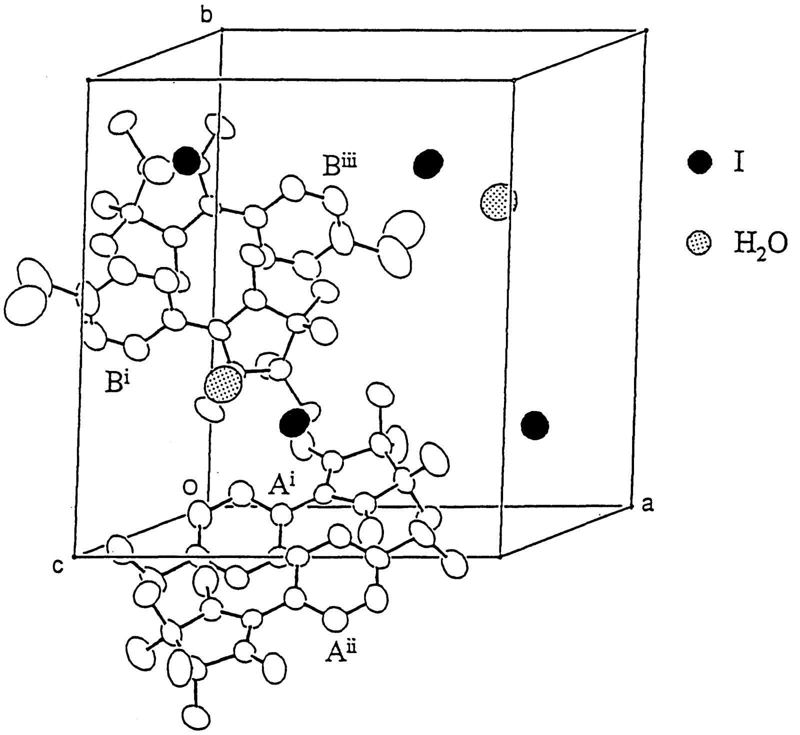


Fig. 2. Solid state structure of **2**. Symmetry operations: (i) x, y, z; (ii) -x+1,-y, -z+2; (iii) -x, -y+1, -z.

There are two crystallographically-independent molecules, **A** and **B**, in the crystal of **2**, while they have little difference in structure. Atom numbering scheme and molecular conformation of **A** are shown in Fig. 1.

There is no significant change in the structure of the nitronyl nitroxide, O1-N2-C3-N2'-O1', between the neutral[2-4] and cation species, and the structure of the pyridinium ring is close to that in *N*-metylpyridinium iodide.[7] In Fig. 2 we show that the solid state structure of **2** consists of two kinds of the dimers, $\mathbf{A}^{i}\cdots\mathbf{A}^{ii}$ and $\mathbf{B}^{i}\cdots\mathbf{B}^{iii}$ (for the symmetry operations, see the caption of Fig. 2). The shorter intermolecular, interatomic distances between $\mathbf{A}^{i}$ and $\mathbf{A}^{ii}$ are 3.09 Å of O1A···C9A, 3.40 Å of O1A···C11A and 3.41 Å of O1A···N10A. The intermolecular overlap between $\mathbf{B}^{i}$ and $\mathbf{B}^{iii}$ is not so large, but it includes the shortest intermolecular distance between the NO groups in the crystal of **2**; 4.16 Å of O1'B···N2'B. The intermolecular overlap between the NO groups has been considered to contribute to the antiferromagnetic coupling.[2]

The EPR g-factors of **2** were determined by using a single crystal. The three principal factors are 2.0048, 2.0062 and 2.0084, giving a square average of $\bar{g}$=2.0065. The g-factor of the powder sample of **1** was also found to be *ca.* 2.007. These values for the cation radicals agree with those of the neutral α-nitronyl nitroxides[8] in which its unpaired electron is localized on the NO groups.[2,6] The g-factors of N-centered radicals are reported to be 2.003— 2.004.[8] The spin densities in **1** or **2** would be localized on the side of the nitronyl nitroxide, as well as in the neutral radicals. MNDO calculation indicated that the total charge in the *N*-ethypyridinium group is +0.92 while +0.08 in the nitronyl nitroxide. The positive charge could be located mainly on the pyridinium ring. The spin and charge are considered to be localized on the two different sites in the molecule of **1** or **2**. The spin-charge separation is characteristic of these α-nitronyl nitroxide cation radicals.

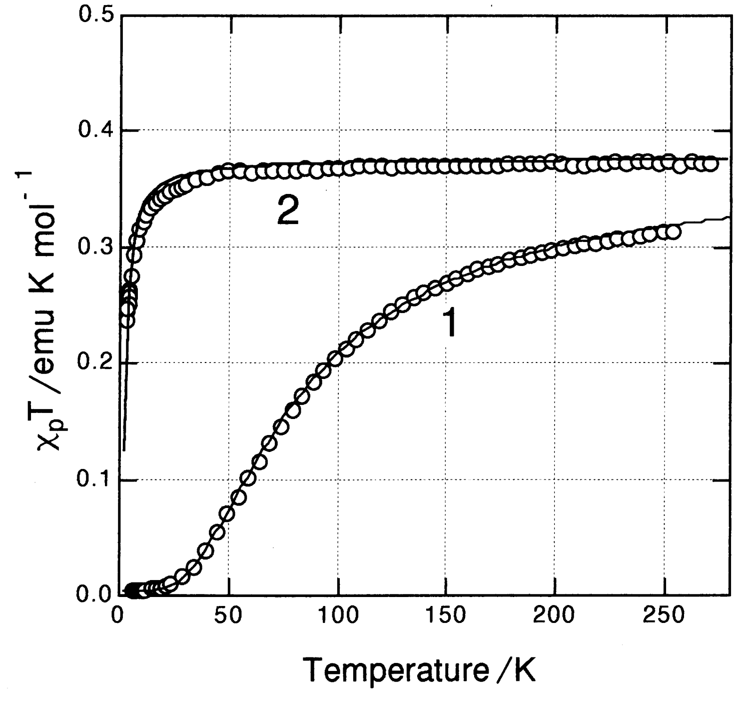


Fig. 3. Temperature dependence of the paramagnetic susceptibility, χ_p, of **1** and **2**. The solid curves are the theoretical fits (see the text).

Temperature dependences of the molar paramagnetic susceptibilities, χ_p, of **1** and **2** are shown in Fig. 3, where $\chi_p T$ are plotted as a function of temperature. $\chi_p T$ of them decrease with decreasing temperature, indicating the antiferromagnetic intermolecular interactions. $\chi_p T$ of **1** are well fitted by the combination of the singlet-triplet model and a small amount of the Curie component due to the lattice defects.9) The solid curve going through the plots for **1** represents the best fit of the experimental data obtained with J_{AF}/k_B=149 K. This coupling constant is larger by two order of magnitude than those in the nitroxide free radicals.2-4) From the magnetic point of view, the nitroxide **1** is concluded to exist as dimers formed by the strong antiferromagnetic interaction. The temperature dependence of χ_p of **2** follows the Curie-Weiss law in the whole temperature range between 3 and 270 K.10) The solid curve fitted to the plots for **2** in Fig. 3, is the theoretical one with the Weiss constant of θ= -1.8 K. The magnetic interaction in **2** is much weaker than that in **1** in spite of their similar molecular structures.

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9) $\chi_p = \frac{N_A g^2 \mu_B^2}{k_B T}\frac{\exp(-J_{AF}/k_B T)}{1+3\exp(-J_{AF}/k_B T)} + \frac{C_{def}}{T}$. The best fit is obtained with g=2.0065(fixed), J_{AF}/k_B=149 K, and C_{def}=4.6x10^{-3} emu K mol^{-1}.

10) $\chi_p = \frac{C}{T-\theta}$. The best fit is obtained with C=0.377 emu K mol^{-1} and θ=-1.8 K.

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