

Clathrate Crystals including the 4-Amino-2,2,6,6-tetramethylpiperidine 1-Oxyl (ATEMPO) Radical as a Guest Component: Change of Magnetic Properties with Host Compounds

Yasuhiro Mazaki,^a Kunio Awaga^b and Keiji Kobayashi*^a

^a Department of Chemistry and ^b Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo, 153 Japan

Two clathrate crystals, one paramagnetic, the other antiferromagnetic, are obtained using the stable radical species ATEMPO (4-amino-2,2,6,6-tetramethylpiperidine 1-oxyl) as a common guest.

There has been much recent interest in organic molecular solids with special magnetic properties, especially in organic ferromagnets.¹ Several different approaches to organic ferromagnetism have inspired numerous molecular designs for spin sources. An organic radical species, when it is included as a guest component in clathrate crystals,² should diversify the intermolecular spin interactions through the host and/or guest molecules in the crystal fields, and hence should provide a

variety of bulk magnetic properties depending on the host compounds. We now demonstrate two clathrate crystals composed of a stable organic free radical 4-amino-2,2,6,6-tetramethylpiperidine 1-oxyl (ATEMPO) as a common guest compound, of which one is paramagnetic, while the other exhibits antiferromagnetic interactions below 4 K. The

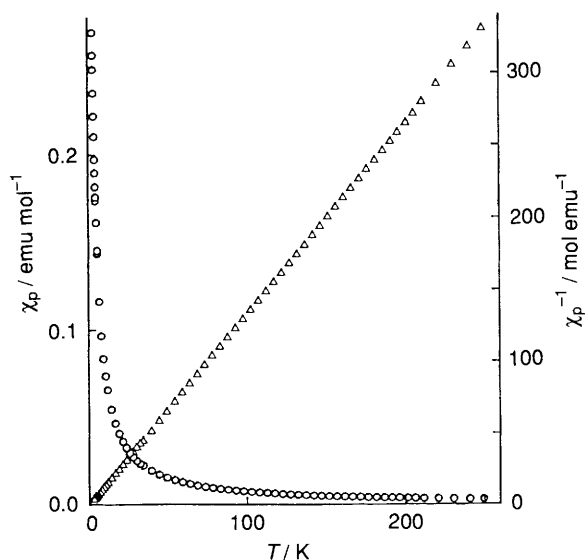


Fig. 1 Temperature dependence of the paramagnetic susceptibility of 1·(ATEMPO)₂

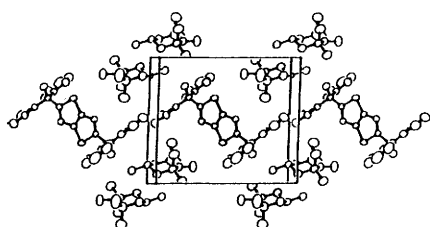


Fig. 2 Stereoview of the crystal structure of the clathrate 1·(ATEMPO)₂ as viewed along the *a* axis

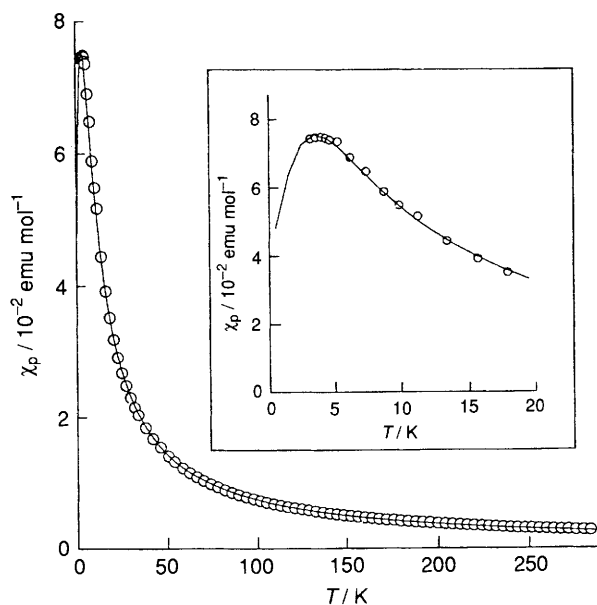
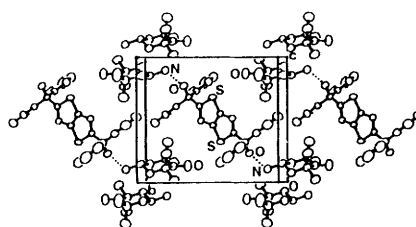


Fig. 3 Temperature dependence of the paramagnetic susceptibility of the powder 2·(ATEMPO)₂. The inset shows the expansion below 20 K.



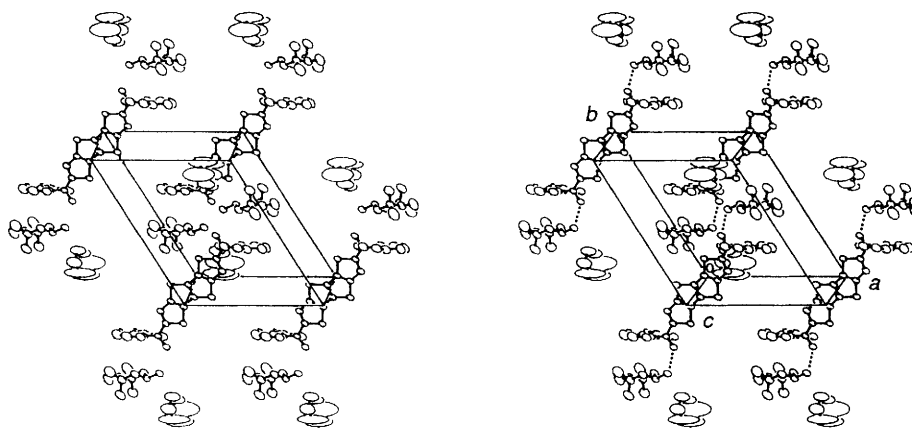


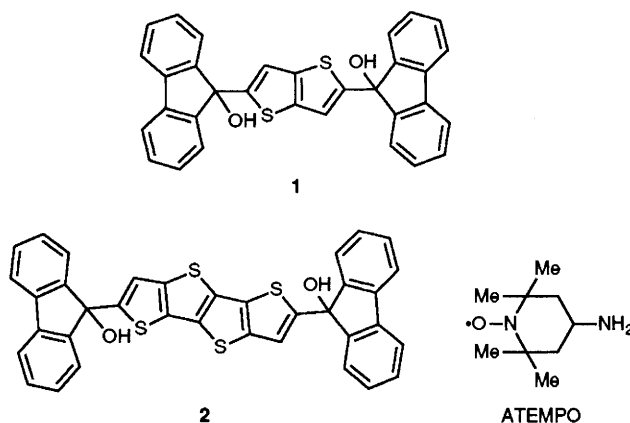
Fig. 4 Stereoview of the crystal structure of the clathrate $2 \cdot (\text{ATEMPO})_2(\text{dioxane})_2$

present study provides the first example, to our knowledge, of inclusion crystals with a stable free radical as a guest of which the solid structure is characterized.

The host compounds employed in this investigation are 9-hydroxy-fluorenyl-substituted polycondensed thiophenes, **1** and **2**, which have been explored in this laboratory.³ The sulfur atoms incorporated in the rigid backbone of the host compounds have been shown to be favourable to intermolecular interactions.⁴ Host **1** afforded a crystalline inclusion complex with a 1:2 stoichiometric ratio for **1**·ATEMPO.

The temperature dependence of the magnetic susceptibility of **1**·(ATEMPO)₂ crystals was measured in the range between 2 and 250 K by the Faraday method. The paramagnetic susceptibility χ_p , after correction of the diamagnetic part, is plotted as a function of temperature in Fig. 1. The temperature dependence of χ_p is found to follow the Curie–Weiss law over the whole temperature range, and the Curie and Weiss constants are determined to be $C = 0.758 \text{ emu K mol}^{-1}$ and $\theta = 0.15 \pm 0.50 \text{ K}$,[†] respectively. The radical concentration was estimated, based on the calculated C value of $0.755 \text{ emu K mol}^{-1}$, to be 100% for the clathrate crystals.

These results indicate that the crystals of **1**·(ATEMPO)₂ are paramagnetic molecular solids with little intermolecular spin-interactions down to liquid-helium temperature. This is reasoned from an X-ray analysis of **1**·(ATEMPO)₂ crystals;[‡] the N–O bonds, that constitute the radical centre, are located far apart from the neighbouring N–O bonds and there are no observed short intermolecular contacts between the host and



guest molecules. The crystal structure is shown in Fig. 2. A host molecule is connected to two guest molecules by the hydrogen bonds to form trimolecular units, which are arranged in a line diagonal to the b and c axes. The O···O and N···N distances between the nearest N–O groups are 7.144 and 7.148 Å, respectively.

When host **2** was recrystallized together with ATEMPO from dioxane, an unstable crystalline complex with a 1:2:2 stoichiometry for **2**·ATEMPO·dioxane was obtained. The guest molecules of dioxane are easily released at room temperature within 2 h. The powders thus formed are composed of an exactly 1:2 stoichiometric ratio of **2** and ATEMPO. The magnetic susceptibility of **2**·(ATEMPO)₂, corrected for the diamagnetic core correction between 3–250 K, fit the Curie–Weiss expression. It decreases, however, at ca. 4 K (Fig. 3), indicating that antiferromagnetic interactions are exerted among the guest radical species.

The magnetostructural correlation cannot be revealed at this stage, since the sample is powder. It was, however, possible to carry out an X-ray crystal analysis for the precursor three-component clathrate crystals by coating the sample crystal with an epoxide adhesive immediately after the filtration of the crystals from a dioxane solution. The X-ray crystal structure is shown in Fig. 4.[‡] The packing motif is essentially the same as that of **1**·(ATEMPO)₂: two ATEMPO molecules are linked by the hydrogen bond to a host molecule. The dioxane molecules are located between the chain of a trimeric unit (ATEMPO)···(**2**)···(ATEMPO). Dioxane has no hydrogen bonds with the other two component compounds. The O···O distance between the nearest radical centre is 5.875 Å and the N···N distance is 6.413 Å.

It seems most likely that, after the collapse of the original crystal lattice by the loss of the dioxane molecules, the N–O bond distances could be arranged to as to facilitate magnetic interactions in **2**·(ATEMPO)₂ solids.

[†] This value seems to indicate a ferromagnetic interaction. However, taking the experimental error into consideration, we are not willing to claim the ferromagnetism based on this result.

[‡] Crystal data for **1**·(ATEMPO)₂: $\text{C}_{50}\text{H}_{58}\text{N}_4\text{O}_4\text{S}_2$, $M = 843.153$, monoclinic, $P2_1/a$, $a = 15.734(2)$, $b = 12.653(2)$, $c = 12.182(2)$ Å, $\beta = 110.46(1)^\circ$ at room temp., $U = 2276.4(6)$ Å³, $Z = 2$, $D_c = 1.231 \text{ g cm}^{-3}$, and $\mu = 1.573 \text{ cm}^{-1}$. 5238 independent reflections with $3 < \theta < 55^\circ$. $R = 0.068$, $R_w = 0.077$ for 3540 unique reflections [$I > 3\sigma(I)$].

Crystal data for **2**·(ATEMPO)₂(dioxane)₂: $\text{C}_{62}\text{H}_{74}\text{N}_4\text{O}_8\text{S}_4$, $M = 1131.529$, triclinic, $P\bar{1}$, $a = 13.764(3)$, $b = 17.336(4)$, $c = 9.220(2)$ Å, $\alpha = 99.47(2)$, $\beta = 100.43(2)$, $\gamma = 122.71(2)^\circ$ at room temp., $U = 1726.5(9)$ Å³, $Z = 1$, $D_c = 1.088 \text{ g cm}^{-3}$, and $\mu = 1.781 \text{ cm}^{-1}$. 7855 independent reflections with $3 < \theta < 55^\circ$. $R = 0.086$, $R_w = 0.13$ for 5433 unique reflections [$I > 3\sigma(I)$]. The rather high R value is ascribable to the thermal motion of dioxane molecules in the inclusion cavity. The dioxane molecules thus show significantly large thermal ellipsoids. These results, along with the low density of the crystals, are consistent with the easy loss of the guest molecules.

For both crystals the data were collected on a Rigaku AFC-5 four-circle diffractometer with monochromatic Mo-K α radiation ($\lambda = 0.71069 \text{ nm}$). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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References

- 1 Y. V. Korshak, T. V. Medvedeva, A. A. Ovchinnikov and V. N. Spektor, *Nature*, 1987, **326**, 370; T. B. Torrance, S. Oostra and A. Nazzari, *Synth. Met.*, 1987, **19**, 708; J. S. Miller, A. J. Epstein and W. M. Reiff, *Chem. Rev.*, 1988, **88**, 201; H. Iwamura, *Adv. Phys. Org. Chem.*, 1990, **26**, 179.
 - 2 J. L. Atwood, J. E. Davies and D. D. MacNicol, *Inclusion Compounds*, Academic Press, London, 1984, vol. 1-3; E. Waber, *Molecular Inclusion and Molecular Recognition—Clathrates I and II*, *Topics in Current Chemistry*, Springer-Verlag, Berlin-Heidelberg, 1987, vol. 140; 1988, vol. 149.
 - 3 Y. Mazaki, N. Hayashi and K. Kobayashi, *J. Chem. Soc., Chem. Commun.*, 1992, 1381; Y. Mazaki, N. Hayashi and K. Kobayashi, *Mol. Cryst. Liq. Cryst.*, 1992, **219**, 75; N. Hayashi, Y. Mazaki and K. Kobayashi, *Chem. Lett.*, 1992, 1689.
 - 4 N. Sato, Y. Mazaki, K. Kobayashi and T. Kobayashi, *J. Chem. Soc., Perkin Trans 2*, 1992, 765; Y. Mazaki and K. Kobayashi, *J. Chem. Soc., Perkin Trans. 2*, 1992, 761.
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