SHORT COMMUNICATIONS

Mechanochemical Spin Generation in a Solid Charge Transfer Complex

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In a previous paper, we have reported on electronic interactions in the solid charge-transfer complexes formed between tetracyanoquinodimethan (TCNQ) and a series of aromatic diamines, and have shown that most complexes can be divided into two main groups according to whether their ground electronic state is non-bonding or ionic.[1] In the course of the study, however, we found that the solid complex of benzidine and TCNQ could not be classified definitely to either of these two groups, as its infrared absorption spectrum was not explained either by a superposition of the spectra of neutral components or by a superposition of the spectra of ionic components.

We report here an interesting phenomenon found during the course of the work to elucidate the character of the ground electronic state of the benzidine-TCNQ system. Solid samples were precipitated from a solution in a similar manner to that described before[1] using several different solvents. Spectroscopic analysis of these solid complexes has indicated that there are two kinds of complexes with respect to occlusion of solvent molecules. The results obtained from the analysis of solution spectra in the UV and visible region are given in Table 1. As an example, the complex prepared in chloroform does not contain any solvent molecule, whereas that prepared in dichloromethane contains solvent molecules in mole ratios of approximately 1 : 1 : 1.5 (benzidine: TCNQ: solvent).*1

These two types of complexes are quite different in their infrared and ESR behaviors. As is shown in Fig. 1, the solid complex composed only of the donor and acceptor molecules exhibits the infrared absorption spectrum well explained by a superposition of the spectra of neutral component molecules, but, in the case of the complexes containing solvent molecules, the spectrum is distinctly different from that for the solvent-free complexes even apart from the bands assigned to the solvent molecules. (See also Fig. 2(c) of Ref. 1.)

TABLE 1. COMPOSITION OF THE BENZIDINE-TCNQ-SOLVENT SYSTEM AS DETERMINED SPECTROSCOPICALLY

Solvent used in preparation	Mol ratio*
$CHCl_3$	1.0 : 1.0 : 0
CH_3CHCl_2	1.0 : 1.1 : 0
CH_2Cl_2	1.0 : 1.1 : 1.6
$(CH_3)_2CO$	1.0 : 0.8 : 0.8
CH_3CH_2Br	1.0 : 1.1 : 1.6

* (Benzidine) : (TCNQ) : (Solvent)

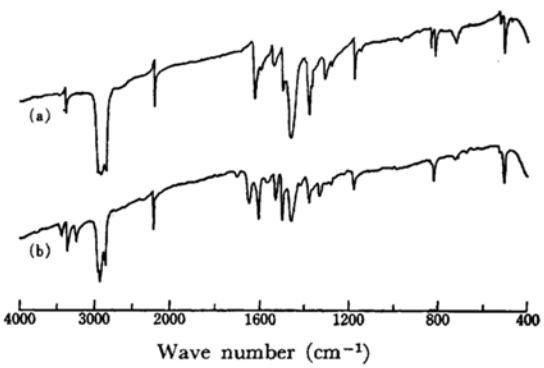

Fig. 1. Infrared absorption spectra of the benzidine - TCNQ complexes; (a) Solvent-free complex and (b) Solvent(acetone)-occluded complex.

In the ESR experiments, a well-grown crystalline sample of benzidine - TCNQ complex containing dichloromethane showed no ESR absorption, but it did give a strong ESR absorption signal (g= 2.0027) when it was ground to fine powder. On the other hand, the solvent-free complexes did not show ESR absorption at all, whether they were ground to fine powder or not.

Preliminary measurements showed that the electrical conductivities for the solvent-occluded samples were always higher by a factor of 10^4—10^5 compared to those for the solvent-free samples. These prominent effects of solvent occlusion on the electronic properties of the system are of great interest and further detailed studies including structural analysis are now in progress in our laboratory.

1) M. Ohmasa, M. Kinoshita, M. Sano and H. Akamatu, This Bulletin, **41**, 1998 (1968).

*1 An elementary analysis resulted in C, 58.45; H, 4.15; N, 15.58; Cl, 18.75, while calculated values for 1 : 1 : 1.5 were C, 59.37; H, 3.71; N, 16.30; Cl, 20.62%.