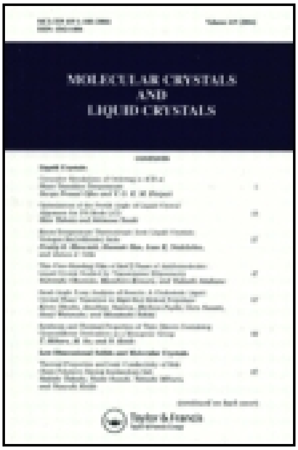

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ESR Studies of One-Dimensional Conductors Based on Tetracyanoquinodimethan (TCNQ)

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ESR STUDIES OF ONE-DIMENSIONAL CONDUCTORS BASED ON TETRACYANOQUINODIMETHAN(TCNQ)

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Abstract ESR studies on a series of polycrystalline tetracyanoquinodimethan(TCNQ) based one-dimensional conductors are described. The donors, all of which are diamagnetic, include alkali metals, alkyl/arylphosphines and substituted bipyridinium compounds. The ESR studies include the measurement of the magnetic susceptibility and the anisotropic g-tensor as a function of temperature. Of particular interest, is the information which one can obtain from a careful study of changes in the g-tensor with respect to changes in the crystal and electronic structures(e.g., phase transitions).

INTRODUCTION

A review of the literature suggests that the g-tensors observed for polycrystalline charge transfer complexes based upon TCNQ are functions of temperature and the identity of the donor, even when the donor is diamagnetic. A purpose of this investigation is to study systematically the effect of temperature, the identity of the donor, and the crystal structure upon the observed g-tensors for a series of TCNQ based charge transfer complexes. It is also a goal to obtain the anisotropic g-tensor for the TCNQ anion radical in order to compare it with calculations made in our laboratory.

EXPERIMENTAL

The ESR measurements were made on a Varian E-12 spectrometer using the dual cavity technique which has been described[1,2]. The values of the principal components of the g-tensor were obtained by the method of Kneubuhl[3]. Under certain circumstances, the "g-tensors" as measured are not the true g-tensors in the strictest interpretation of the meaning of that concept but the effective g-tensor. However, we have found it useful to treat all data obtained as if they represented the true g-tensor. The charge transfer complexes which have been studied and are reported upon here are shown below.

1. KTCNQ
2. Triphenylmethylarsonium(TCNQ)$_2$
3. Triphenylmethylphosphonium(TCNQ)$_2$
4. Diphenyldimethylphosphonium(TCNQ)$_2$
5. Diphenyldiethylphosphonium(TCNQ)$_2$
6. 1,1'-Bis(p-cyanophenyl)-4,4'-bipyridinium(TCNQ)$_4$
7. 1,1'-Bis(p-methylphenyl)-4,4'-bipyridinium(TCNQ)$_4$

RESULTS

Figure 1 shows a plot of the principal components of the g-tensor for KTCNQ against temperature. KTCNQ was chosen for display because it illustrates most of the important points which we wish to emphasize in this paper. The paramagnetic species which is observed at temperatures above 300 K is the mobile triplet exciton which lies 0.24 ev above the singlet ground state[4]. For temperatures above 300 K there is relatively little dependence of the principal components upon temperature. However, KTCNQ undergoes a phase change at ca. 395 K(shown by the dotted line in the Figure) which causes

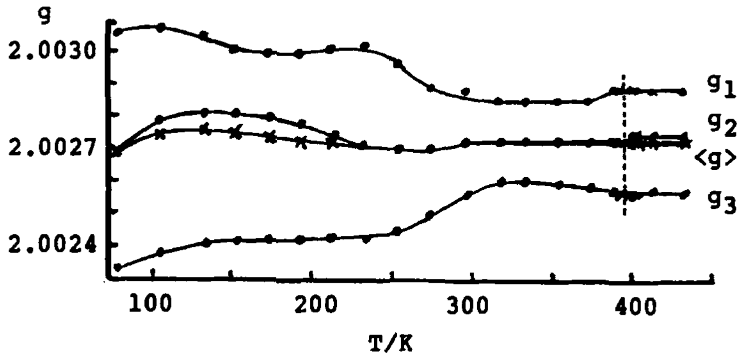

FIGURE 1 Plot of g-tensor vs temperature.

an abrupt change to be observed in the lineshape and hence in the observed g-tensor components. Between 300 and 250 K the number of triplet excitons drops from 10% to 3% of the number present at 430 K. Between 250 and 200 K the drop is from 3% to 1%. In the latter range, there is a strong dependence upon temperature of the g-tensor measured from the spectral envelope because one is looking at the superposition of at least two radicals which are present at approximately equal concentrations. Below 200 K, one is looking at what we believe are trapped, or nearly trapped, randomly oriented TCNQ anion radicals. Even at the lowest temperatures of this study it appears there may be yet a temperature dependence of the g-tensor which suggests that lower temperature measurements should be made. Such measurements are planned.

At the lowest temperature of the study(i.e., 77 K), for all the other complexes, the lowest concentration of paramagnetic species is considerably greater than for KTCNQ. In terms of Figure 1, at 77 K, for each of the complexes, there is a shift to the right which is inversely proportional to the value of the activation energy which describes the complex. For example, for complexes #2 and #4, with J's of 0.085 and 0.039, the equivalent points on Figure 1 are 217 and 474 K, respectively.

Table 1 shows the temperature dependence of the magnetic susceptibility for the complexes in this study.

TABLE 1 Temperature dependence of magnetic susceptibility for the complexes studied.

Complex	Temp. Dep.	Act. Engy./ev[5]	Ref.
1	sing./trip.	0.24	4
2	sing./trip.	0.085($\pm$3)	6
3	sing./trip.	0.085($\pm$3)	6
4	sing./trip.	0.039($\pm$3)	7,8
5	activated	0.0092($\pm$6)	7
6	Curie Law	-	6
7	-	-	-

CALCULATIONS

The anisotropic g-tensors for the TCNQ anion radical were calculated using the Engery Weighted Maximum Overlap(EWMO) technique which was first proposed by

Linderberg and Ohrn[9]. For more information, regarding the use of this technique and an example of its use, see Jones and de Boer[10]. The molecular structure data were taken from references 7 and 11. The molecular axis system is defined as follows: x is along the long axis, y is along the short axis and z is perpendicular to the molecular plane. The calculated principal components of the TCNQ anion radical are shown in Table 2 in comparison with experimental values obtained from KTCNQ at 77 K.

TABLE 2 Calculated and experimental g-tensors.

	Calculated	Experimental
$g_{xx}(g_2)$	2.003152	2.00269(±1)
$g_{yy}(g_1)$	2.003450	2.003055(±5)
$g_{zz}(g_3)$	2.002319	2.00232(±2)
$\langle g \rangle$	2.002974	2.00269(±1)

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