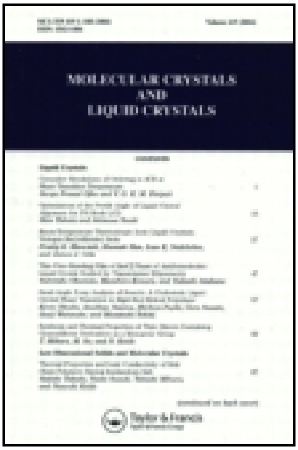

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Solvent-Inclusion Effects on the Structures and Properties of Molecular Complexes and Radical Salts

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Solvent-Inclusion Effects on the Structures and Properties of Molecular Complexes and Radical Salts

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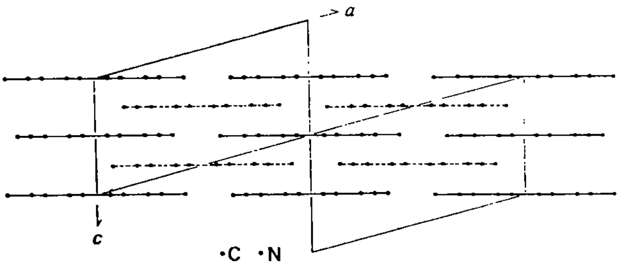
Some molecular complexes and radical salts give the crystal forms which contain solvent molecules in their crystal lattices, and these solvated crystals often exhibit physical properties markedly different from those of the solvent-free crystals. Two typical examples of such cases, on which we have recently investigated, will be described here to illustrate the characteristic features of solvent-inclusion.

BENZIDINE-TCNQ COMPLEX

Various solvent molecules can enter into the crystal lattice of this complex to give the solvated modifications.[1–3] The crystal structures of these modifications of BD·TCNQ complex can be classified into three types; Type I is the structure of the solvent-free modification (Figure 1a), type II that is commonly found in the cases which contain aliphatic compounds such as dichloromethane and acetonitrile, and type III that is found in the cases which contain benzene or its derivatives.

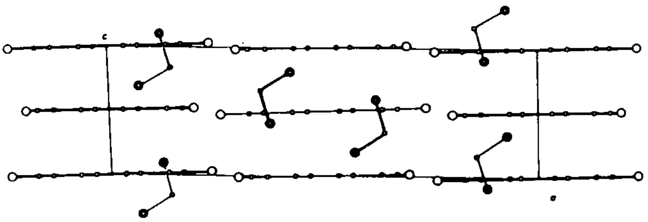
In every case, benzidine and TCNQ molecules are alternately stacked on each other to form molecular columns as it is generally found in charge-transfer complexes, but, in the cases of type II and type III, there are channels between these columns to accommodate solvent molecules. Intermolecular hydrogen bond is likely to play an important role in stabilizing the channel structures of solvated crystals.

When a solvated crystal is kept in the ordinary atmosphere at room temperature, the solvent molecules are partially lost from the crystal creating vacancies at solvent sites.



projection to (010) plane

FIGURE 1a BD·TCNQ (type I)



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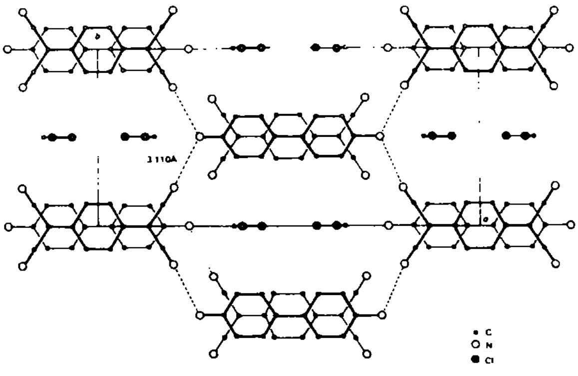
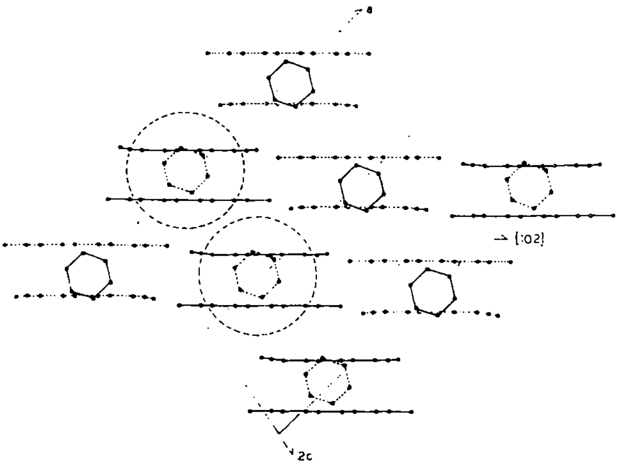
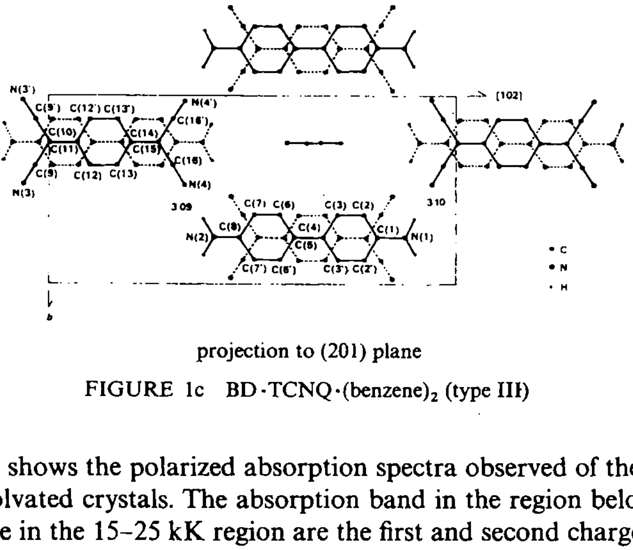


projection to (001) plane

FIGURE 1b BD·TCNQ·$(CH_2Cl_2)_{1.8}$ (type II)



projection to (010) plane



projection to (201) plane

FIGURE 1c BD·TCNQ·(benzene)$_2$ (type III)

Figure 2 shows the polarized absorption spectra observed of the solvent-free and solvated crystals. The absorption band in the region below 15 kK and the one in the 15–25 kK region are the first and second charge-transfer bands, respectively. The first charge-transfer band is polarized parallel to the crystal axis along which benzidine and TCNQ molecules are alternately stacked, whereas the second one is polarized perpendicular to this axis because of the strong mixing with an intramolecular excitation. Both of these charge-transfer bands are appreciably affected by solvation.

The electrical conductivity data are listed in Table I. The room temperature conductivity is markedly higher in the solvated modifications as compared with the solvent-free one. It should be noted also that there

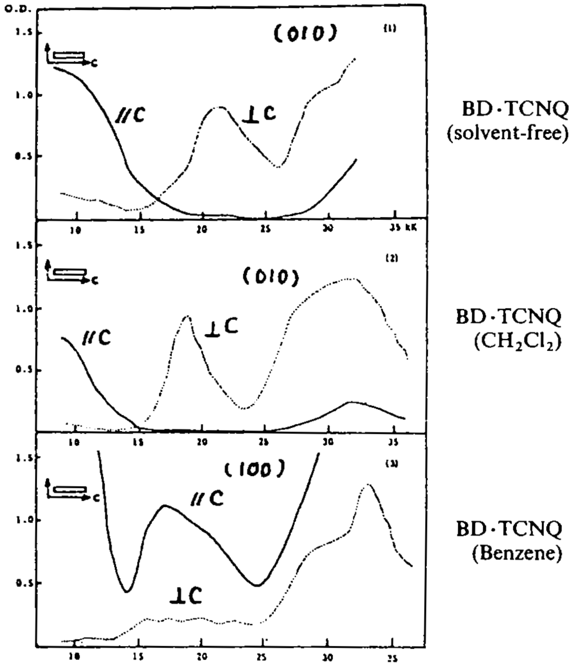


FIGURE 2 Crystal spectra of solvent-free and solvated forms of BD·TCNQ.

TABLE I

Solvent	σ (ohm^{-1} cm^{-1})[a]	E(eV)
Type I		
solvent-free	1×10^{-9}	0.54
Type II		
CH_2Cl_2	1×10^{-6}	0.11
C_2H_5Br	2×10^{-4}	0.12
CH_2ClCH_2Cl	1×10^{-4}	0.14
CH_3CN	1×10^{-5}	0.16
CH_3COCH_3	3×10^{-6}	0.21
Type III		
C_6H_6	1×10^{-6}	0.28
C_6H_5Cl	3×10^{-7}	0.38
C_6H_5Br	1×10^{-7}	0.40
$C_6H_5CH_3$	3×10^{-8}	0.43
C_6H_5CN	2×10^{-9}	0.44
$C_6H_5NO_2$	3×10^{-9}	0.50

[a] Room temperature conductivity.
[b] Activation energy.

is a considerable difference as regards the magnitude of conductivity between type II and type III.

ALKALI METAL-CHLORANIL OR -BROMANIL SALTS

The $K^+ \cdot CA^-$ salt has the crystal structure where CA^- ions are stacked on each other to form one-dimensional chains of CA^- ion along *c*-axis, and K^+ ions are located in the space between such CA^- columns.[4] The powder of $K^+ \cdot CA^-$ changes to the hydrous state when kept in the ordinary atmosphere, but is reversibly converted to the anhydrous state when kept in vacuum.[5] Similar phenomena were found also for $Na^+ \cdot CA^-$ and $Na^+ \cdot BA^-$, but not for $K^+ \cdot BA^-$.

The optical properties of the above salts markedly change on hydration. Figure 3 shows the difference of crystal spectrum between the anhydrous and hydrous state. The following conclusions have been derived from the

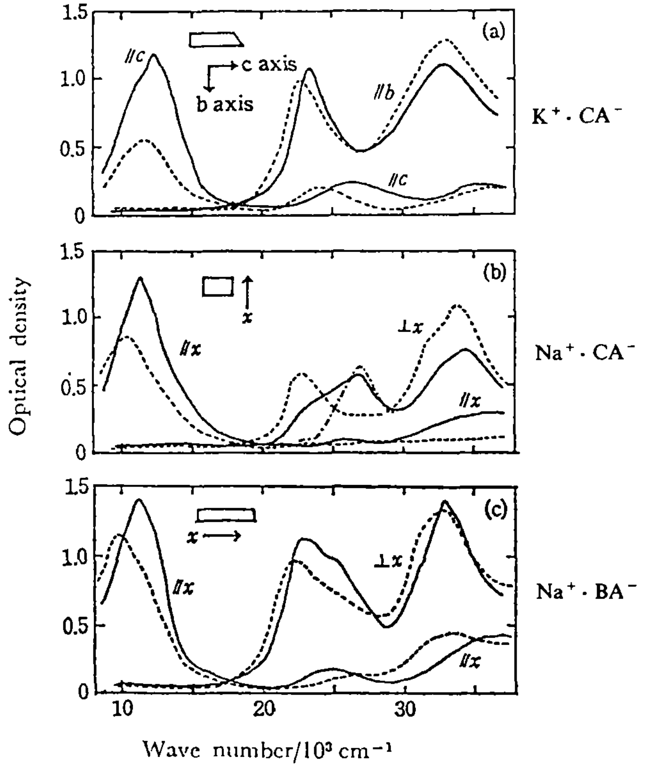


FIGURE 3 Crystal spectra of anhydrous (----) and hydrous states (——).

examination of the crystal spectra; (i) The one dimensional chain of CA^- (or BA^-), which exists in the crystal structure of the anhydrous state, is preserved also in the hydrous state, but (ii) CA^- (or BA^-) ions in such a chain are taking a dimeric array in the case of the hydrous state, with a stronger charge-transfer interaction between the neighboring ions.

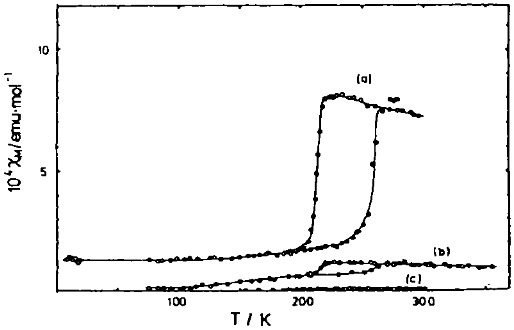


FIGURE 4 Intrinsic paramagnetism of $K^+ \cdot CA^-$; (a) anhydrous state; (b) (c) hydrous states.

A marked decrease of paramagnetic susceptibility is caused by hydration. In particular, drastic change is observed in the case of $K^+ \cdot CA^-$.[5,6] The paramagnetic susceptibilities of the anhydrous and hydrous states of this salt are shown in Figure 4. The anhydrous salt exhibits a phase transition in the temperature region of 210–270 K, where the salt changes from the low-spin state to the high-spin state,[7] but no corresponding transition can be observed in the case of the hydrous salt, showing a quite low paramagnetism over the temperature range of 70–300 K. This phenomenon is likely to be due to the strong stabilization of the singlet ground state associated with the charge-transfer interaction between the neighboring CA^- ions in the hydrous state.

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